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ELECTRON TRANSLATION FACTORS
AND THE
DETERMINATION OF SWITCHING FUNCTIONS

by

Ⓒ JOHN RANKIN

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH

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FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled ELECTRON TRANSLATION FACTORS AND THE DETERMINATION OF SWITCHING FUNCTIONS submitted by JOHN RANKIN in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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ABSTRACT

This thesis presents a scheme for correcting certain fundamental errors in the perturbed stationary states theory of slow atomic collisions. The corrections are associated with electron translation factors, of which the pss theory gives no account. In the corrected theory, switching functions are used ~~to~~ describe electron translation in a molecular state. One can use a single function for all electronic states, or each state may have its own, characteristic switching function. However, the functions are not fully specified by the theory, and the choice of suitable ones is an important practical problem. This thesis examines one method of choosing them, based on the fact that the corrected nonadiabatic couplings for ionising transitions are very sensitive to the choice of switching function. For each bound electronic state, it is possible to choose an "optimum" switching function, such that the corrected couplings are very much smaller, and of shorter range, than those predicted by pss theory. These results are compared with those obtained using simpler choices.

Ionisation matrix elements are presented for the system of one electron and two nuclei, notably for H_2^+ and HeH^{++}, and the parameters specifying the switching functions for the lowest bound states are given. The implications of these results for nonadiabatic couplings in general are also discussed.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF ILLUSTRATIONS

CHAPTER I

INTRODUCTION

A. Aims and Objectives

This thesis presents a scheme for correcting certain fundamental errors in the well-known and widely used perturbed stationary states (pss) theory of slow atomic collisions. The corrections in question are associated with electron translation factors, of which pss theory gives no account. The corrected theory has been developed by Thorson[1,2] and others[3-6] and has recently been formalised by Thorson and Delos,[7] who use switching functions to describe electron translation in a molecular state. These functions are not fully specified by the theory, and the choice of suitable ones presents an important practical problem. This thesis explores one method of choosing them, based on the fact that nonadiabatic couplings (corrected for electron translation effects) are extremely sensitive to the choice of switching function, especially for ionising transitions.[1,2] I show that it is possible to choose an "optimum" switching function, characteristic of each bound electronic state, such that the corrected coupling matrix elements are very much smaller, and of shorter range, than those predicted by pss theory. I also compare these results with those obtained using simpler choices[3] for the switching function. For truly "molecular" states, the "optimum" switching functions lead to significantly better results, while for purely "atomic" states, the method selects the simpler functions quite naturally.

Detailed ionisation matrix elements are presented for the system of one electron and two nuclei, especially for H_2^+ and HeH^{++}, and the parameters specifying the switching functions for the lowest electronic bound states are given. The implications of these results for nonadiabatic couplings in general are also discussed.

In the rest of the Introduction, I shall explain the meaning of the terms used above, review the history of the problem and provide signposts to guide the reader through the detail, which would otherwise obscure the main ideas of the dissertation.

B. Background Material

1. Basics

The problem of interest to us occurs in all atomic and molecular collisions, but its essential features can be studied most easily in the model systems considered here, composed of two heavy particles, masses M_A, M_B, and charges Z_Ae, Z_Be, and an electron, mass m_0. After separating out the centre of mass motion, we require, in principle, the solution to the time-independent Schrödinger equation,

$$H(\vec{r},\vec{R})\ \Psi(\vec{r},\vec{R}) = E\ \Psi(\vec{r},\vec{R}), \tag{I-1}$$

subject to the appropriate scattering asymptotic boundary conditions. *Molecular* co-ordinates, $\vec{R}$, $\vec{r}$, are used: $\vec{R}$ is the vector from A to B, and $\vec{r}$ is the position vector of the electron from the centre of mass of the nuclei. For the moment, we express $\vec{r}$ in terms of reference axes fixed in space, but, later on, it will be more convenient to use a frame rotating with the molecular axis $\vec{R}$. The reader should pay careful attention to the subject of co-ordinates, because it is closely related to the central problem of the thesis: in an atomic collision, the system separates asymptotically into two *atomic* subsystems, for which atomic, rather than molecular, co-ordinates are more appropriate; and the transformation of wavefunctions from one co-ordinate system to the other is not quite as trivial as it seems.

In molecular co-ordinates, the Hamiltonian, $H(\vec{r},\vec{R})$, is

$$H(\vec{r},\vec{R}) = -\ (\hbar^2/2\mu)\ (\vec{\nabla}_R{}^2)_{\vec{r}} + h_e(\vec{r};\vec{R}), \tag{I-2a}$$

$$\mu = M_A M_B/(M_A+M_B)\ ; \tag{I-2b}$$

$h_e(\vec{r};\vec{R})$ is the molecular electronic Hamiltonian,

$$h_e(\vec{r};\vec{R}) = -(\hbar^2/2m)\ (\vec{\nabla}_r{}^2)_{\vec{R}} + V(\vec{r};\vec{R}), \qquad \text{(I-3a)}$$

$$m = m_0(M_A+M_B)/(M_A+M_B+m_0), \qquad \text{(I-3b)}$$

and $V(\vec{r};\vec{R})$ is the electrostatic potential energy,

$$V(\vec{r};\vec{R}) = (Z_A Z_B e^2/R) - (Z_A e^2/r_A) - (Z_B e^2/r_B). \qquad \text{(I-4)}$$

For a wide range of physical conditions, the *classical trajectory approximation*,[8,9] in which only the electron motion is treated quantum mechanically, provides an alternative to solving equation (I-1). The nuclei are assumed to follow some specified classical trajectory $\vec{R}(t)$, and the electronic wavefunction obeys the time-dependent Schrödinger equation,

$$h_e\{\vec{r};\vec{R}(t)\}\ T(\vec{r},t) = i\hbar\ \{\partial T(\vec{r},t)/\partial t\}_{\vec{r}}. \qquad \text{(I-5)}$$

We shall make use of both descriptions of a slow collision in this thesis; for nearly all problems of interest to us, the two approaches give the same final results.

In general, equations (I-1) or (I-5) are solved by expanding the wavefunction in terms of some appropriate set of electronic states, $|n(\vec{R})\rangle$, projecting out the j'th component with $\langle j(\vec{R})|$, and solving the resulting coupled equations. In principle, any complete set of functions will do, but, in practice, the set is always truncated, and the idea is to choose a set which approximates the true behaviour as closely as possible.

If the nuclear speed is much less than the electron speed, we may expect that the electron system will adjust smoothly to changes in the nuclear position; this is the fundamental assumption of the Born-Oppenheimer approximation in molecules, and the same idea can be used in <u>slow collision theory</u>. At each nuclear configuration, the set of Born-Oppenheimer (fixed-nuclei), adiabatic states may be used as the expansion basis. These states are eigenfunctions of the electronic Hamiltonian,

$$h_e(\vec{r};\vec{R})\ \phi_n(\vec{r};\vec{R}) = \varepsilon_n(R)\ \phi_n(\vec{r};\vec{R}); \qquad \text{(I-6)}$$

they depend parametrically on $\vec{R}$, and coupling between them occurs via this dependence. If the system evolves nearly <u>adiabatically</u>, coupling is unimportant, and elastic scattering on the potentials $\varepsilon_n(R)$ dominates. Conditions for the validity of adiabatic approximations are usually discussed using the time-dependent Schrödinger equation; it can be shown that the condition for adiabatic evolution is[10]

$$|\vec{v}\cdot\langle j|\vec{\nabla}_R h_e|n\rangle| \ll |\epsilon_n\{R(t)\}-\epsilon_j\{R(t)\}|/\hbar, \qquad \text{(I-7)}$$

where $\vec{v} = d\vec{R}/dt$ is the nuclear velocity.

We can now define the term "slow collision" more precisely: a collision is said to be slow if the adiabatic criterion is satisfied for "principal quantum transitions" --transitions for which $\Delta\epsilon > 1.0$ eV. For $M_A \simeq M_B$ equal to the proton mass, collision energies below about one keV are slow. However, note that, even if $\vec{v}$ is very small, the adiabatic criterion will be violated in the case of coupled, nearly degenerate states. This means that some states of an atomic collision system can never behave adiabatically, i.e., the continuum electronic states and the closely spaced, Rydberg levels; even for the more tightly bound states, strong nonadiabatic coupling can occur if a local near-degeneracy $\epsilon_j(R_0) \simeq \epsilon_n(R_0)$ of two potential curves is encountered.

Slow collision processes may thus be divided into two broad categories:

a. Direct impact processes, for which $|\epsilon_j-\epsilon_n|$ is large, and the nuclear momentum change accompanying a transition is large; such transitions are improbable, and the system evolves nearly adiabatically (e.g., impact ionisation of low-lying, bound-state electrons)

b. Degeneracy mediated processes, in which the adiabatic criterion is locally violated, due to near-degeneracy of two (or more) levels, and the transition probabilities are large, even at low collision velocities (e.g., avoided crossings of adiabatic potential curves) An adequate theory of slow collisions should be able to describe both categories.

2. PSS Theory

The perturbed stationary states (pss) method[11] takes a truncated set of Born-Oppenheimer electronic wavefunctions as the expansion basis; thus, for equation (I-1),

$$\Psi(\vec{r},\vec{R}) = \sum_{n}^{N} \chi_n(\vec{R}) \; |n(\vec{R})>, \qquad \text{(I-8a)}$$

$$|n(\vec{R})> = \phi_n(\vec{r};\vec{R}). \qquad \text{(I-8b)}$$

One then obtains coupled equations for the functions $\chi_n(\vec{R})$ as components of an abstract vector $\underline{\chi}(\vec{R})$:

$$(1/2\mu) \; \{-i\hbar \, \vec{\nabla}_R + \underline{P}(\vec{R})\}^2 \; \underline{\chi}(\vec{R}) + \underline{\varepsilon}(R) \; \underline{\chi}(\vec{R})$$

$$= E \, \underline{\chi}(\vec{R}). \qquad \text{(I-9)}$$

The matrix, $\underline{\varepsilon}(R)$, is diagonal, and its nn element is the potential curve, $\varepsilon_n(R)$; coupling between states j and n arises solely from the nonadiabatic coupling matrix, $\underline{\vec{P}}(R)$,

$$\vec{P}_{jn}(R) = -i\hbar <\phi_j|(\vec{\nabla}_R)_{\vec{r}}|\phi_n>. \qquad \text{(I-10)}$$

It can be shown that $\vec{\underline{P}}(R)$ is Hermitian and that its diagonal elements vanish. To derive equation (I-9), I have used the relation

$$-i\hbar\,\{\vec{\nabla}_R\cdot\vec{\underline{P}}(R) + \vec{\underline{P}}\cdot\vec{\underline{P}}\}_{jn} = \langle\phi_j|-\hbar^2(\nabla_R{}^2)_{\vec{r}}|\phi_n\rangle. \quad \text{(I-11)}$$

Note that the gradient in (I-10) is computed holding $\vec{r}$ fixed in the non-rotating frame, which accounts for the existence of angular, as well as radial, components in the vector, $\vec{\underline{P}}(R)$. In actual calculations, we use a frame rotating with the molecular axis to describe the electron system; in this frame, the Hamiltonian, h_e, and the basis states, ϕ_n, depend only on $R = |\vec{R}|$, and the angular parts of $\vec{P}_{jn}$ arise directly from the transformation from $\vec{r}$ (nrf) to $\vec{r}\,'$ (rf). Physically, these terms represent the Coriolis interaction.

In the alternative, classical trajectory description, the analogous pss expansion is[12]

$$T(\vec{r},t) = \sum_n a_n(t)\;\phi_n\{\vec{r};\vec{R}(t)\}\;\exp\{-i\textstyle\int^t\varepsilon_n(t')dt'/\hbar\}; \quad \text{(I-12)}$$

the resulting coupled equations for the amplitudes, $a_n(t)$, are

$$i\hbar\; da_j/dt = \sum_n \vec{v}\cdot\vec{P}_{jn}\;a_n(t)\;\exp\{-i\textstyle\int^t(\varepsilon_n-\varepsilon_j)dt'/\hbar\}, \quad \text{(I-13)}$$

where we have used the relation

$$-i\hbar\,[\partial\phi_n\{\vec{r};\vec{R}(t)\}/\partial t]_{\vec{r}} = -i\hbar\,\vec{v}.(\vec{\nabla}_R)_{\vec{r}}\,\phi_n(\vec{r};\vec{R}). \qquad \text{(I-14)}$$

Notice that, in both this approach and that of equation (I-9), transitions arise from the same nonadiabatic coupling matrix, $\underline{\vec{P}}(R)$. The connection between this matrix and the adiabatic criterion can be seen from the relation

$$\begin{aligned}\vec{P}_{jn}(R) &= -i\hbar\,\langle\phi_j|(\vec{\nabla}_R)_{\vec{r}}|\phi_n\rangle \\ &= -i\hbar\,\langle\phi_j|(\vec{\nabla}_R h_e)_{\vec{r}}|\phi_n\rangle/(\epsilon_n-\epsilon_j). \qquad \text{(I-15)}\end{aligned}$$

Nonadiabatic couplings arise from the changes in, or perturbations of, the adiabatic states, as the nuclear configuration alters (hence the name, "perturbed stationary states" theory). The presumption, of course, is that the matrix, $\underline{\vec{P}}(R)$, really does represent the effects of physical changes in the wavefunctions. However, this presumption is not correct, as I shall now explain.

3. Electron Translation Factors

In order to understand why pss theory does not provide an adequate description of slow collision processes, we start by examining the asymptotic ($R\to\infty$) behaviour of the system. Suppose that the electron is in a bound atomic state on nucleus B, asymptotically, and that this "B-atom" is translating with respect to some origin. Seen from this origin, the electron will undergo not only its internal "atomic orbital motion," but also a <u>translational motion</u>, due to the motion of the nucleus to which it is bound. Hence, if the CMN is the origin of electron co-ordinates (as in the molecular system, $\vec{R}$, $\vec{r}$), then the wavefunction <u>must</u> include a factor to describe the translational motion of the electron with respect to the CMN.

However, pss theory gives no account of this factor at all: the Born-Oppenheimer electronic states contain no information about the collision velocity, and the $\chi_n(\vec{R})$'s in equation (I-8a) are "nuclear wavefunctions" and independent of the electron co-ordinates. Effects of electron translation must somehow be buried in the matrix, $\underline{\vec{P}}(R)$, which we may therefore expect to show some unexpected (and undesirable) features.

If the electron is in an atomic state, n, on nucleus B, its internal motion can be described by the atomic orbital $\phi_n^B(\vec{r}_B)$, where $\vec{r}_B$ is the vector from B to e^-. Asymptotically, this orbital is totally unperturbed by the distant nucleus, A, and, if $\underline{\vec{P}}(R)$ is to represent <u>real</u> non-adiabatic couplings, we would therefore expect all the matrix elements of $\underline{\vec{P}}(R)$ to tend to zero, as $R \to \infty$.

In fact, $\underline{\vec{P}}(R)$ does <u>not</u> become zero, as $R \to \infty$; moreover, the non-zero elements, $\vec{P}_{jn}(\infty)$, can be shown to arise from simply displacing the orbital, $\phi_n^B(\vec{r}_B)$, with respect to the CMN, without deforming it at all. These displacement terms are wholly spurious. Unfortunately, they are also often large; indeed, in some cases, they dominate even at finite R-values. A good illustration of this is provided by the matrix elements of $\underline{\vec{P}}(R)$ connecting bound molecular states to the Born-Oppenheimer electronic continuum (it can be shown[1] that such couplings are related to the direct-impact ionisation cross sections). For these transitions, all elements, $\vec{P}_{jn}(R)$, go to zero asymptotically, but, in the interaction region, they are physically unrealistic:[2] typically, each bound state is coupled to 30 or 40 continuum partial waves, and the envelope of couplings extends to at least 40 au. One of the aims of this thesis is to show that a careful choice of the "electron translation factor" eliminates most of these couplings entirely.

A further problem with pss theory appears if we examine $\underline{\vec{P}}(R)$ for a system in which $M_A \neq M_B$. Because the reference origin is the CMN, $\underline{\vec{P}}(R)$ contains terms at all R-values, which depend directly on the nuclear mass asymmetry, to <u>zero'th</u> order in (m/μ). But, in actual fact, the electron "sees" only the electrostatic potential of the nuclei in $h_e(\vec{r};\vec{R})$, and the only information about the nuclear masses that can appear is in the electronic reduced mass, as a correction of <u>first</u> order in (m/μ). This anomaly also occurs because of the neglect of electron translation, and has been discussed in great detail for HD^+ by Davis and Thorson.[13]

Clearly, the matrix, $\vec{\underline{P}}(R)$, does not represent simply the effects of real change in the electronic wavefunctions, and the theory needs to be corrected. To see how this can be done, we examine the form of the "electron translation factor" which appears in the wavefunction asymptotically. If the electron is attached to B, and B is moving at a constant velocity, $\vec{w}_B$, with respect to the CMN, then (in the time-dependent language of equation (I-5)) the electron translation factor (etf) is just

$$F_B = \exp\{(im/\hbar)\ (\vec{w}_B.\vec{r} - \tfrac{1}{2}\, w_B^{\ 2}\ t)\}, \qquad \text{(I-15a)}$$

and the asymptotic electronic wavefunction is not simply $\phi_n^{\ B}(\vec{r}_B)$, but

$$\Phi_n^{\ B} = F_B\ \phi_n^{\ B}(\vec{r}_B). \qquad \text{(I-15b)}$$

The factor, F_B, represents just the momentum and kinetic energy of an electron moving with velocity, $\vec{w}_B$, with respect to the CMN. Similarly, if the electron is bound to A, there is a corresponding factor, F_A, and velocity, $\vec{w}_A$.

However, in the interaction region, the form of the etf is not so clear. In a slow collision, we want to describe the electron motion in terms of the Born-Oppenheimer wavefunctions. Now, at finite R-values, these states are "molecular," rather than "atomic," in character, and it is not possible to say that the electron is attached to a particular nucleus. Rather, when the electron is near nucleus A, it is carried along by A; and, when it is near B, it translates with B. Thus, an electron in a molecular state requires a "molecular" etf, and the idea of a switching function was introduced[6] to give the electron a local translational velocity, as a function of its position. Using this idea, it can be shown[7] that a formally correct theory of slow collisions can be constructed, which removes all the defects of pss theory, while retaining much of its simplicity.

4. Switching Functions and Translation Factors

The rigorous, fully quantum mechanical derivation of the correct coupled equations to replace (I-9) is very subtle.[7b] The defects of pss theory are shown to arise from an inadequate choice of co-ordinates, $(\vec{r},\vec{R})$, in which to separate the internal, "electronic" motion and the translational, "heavy-particle" motion. If one carefully selects a "scattering co-ordinate," $\vec{\xi}$, to replace $\vec{R}$, the (non-linear) transformation from $(\vec{r},\vec{R})$ to $(\vec{r},\vec{\xi})$ introduces important new terms into the coupled equations, terms which remove all the defects of pss theory.

In this thesis, however, I prefer to use an alternative derivation, based explicitly on the etf concept,[7a] which brings out more clearly the main physical ideas. I will show that the etf arises naturally from the boundary conditions satisfied by Ψ (or T) at large R, and that all the problems with pss theory can be solved by attaching an appropriate etf to each Born-Oppenheimer state. The simplest derivation of new coupled equations assumes the classical trajectory approximation.[8,9] It will turn out that a suitable expansion basis is given by the set

$$|n(\vec{R})> = \phi_n(\vec{r};\vec{R}) \exp[(im/\hbar)\ \{\vec{v}.\vec{s}-\int^t (1-\lambda^2)v^2 dt'/8\}], \qquad \text{(I-16)}$$

where

$$\vec{s}(\vec{r};\vec{R}) = \tfrac{1}{2}\ \{f(\vec{r};\vec{R})+\lambda\}\ \vec{r}_g \qquad \text{(I-17a)}$$

$$\vec{r}_g = \vec{r} - \tfrac{1}{2}\ \lambda\ \vec{R} \qquad \text{(I-17b)}$$

and λ is the mass asymmetry parameter,

$$\lambda = (M_A-M_B)/(M_A+M_B). \qquad \text{(I-17c)}$$

$f(\vec{r};\vec{R})$ is called the molecular switching function, and it allows the translational motion of the electron to vary with its position in the molecule. To meet the boundary conditions, as $R \to \infty$, f must approach +1, if the electron is in a bound state of B; and -1, if it is bound to A; but it is otherwise unconstrained. The question of how f should be chosen in the interaction region will be discussed at length, and one scheme for doing so is the main topic of this thesis.

Inclusion of the etf leads to important modifications in the coupled equations, (I-9) or (I-13), the main one being the replacement of the matrix, $\underline{\vec{P}}(R)$, by the corrected nonadiabatic coupling matrix, $\underline{\vec{P}}(R)+\underline{\vec{A}}(R)$, where

$$\vec{A}_{jn}(R) = (im/\hbar)\ \langle\phi_j|[h_e, s(\vec{r};\vec{R})]|\phi_n\rangle. \qquad \text{(I-18)}$$

The λ-dependent term in $\underline{\vec{A}}(R)$ exactly cancels the spurious effects of mass asymmetry in $\underline{\vec{P}}(R)$, and transfers the origin of electron co-ordinates to the geometric centre ($\vec{r}_g$ is the corresponding co-ordinate). In the limit, $R \to \infty$, the term containing f removes the spurious asymptotic couplings, and, in effect, refers the origin of co-ordinates to the nucleus to which the electron is actually bound.

5. Ionising Transitions

In the earlier discussion of the adiabatic criterion, I pointed out that electronic continuum states cannot evolve adiabatically. This means that ionisation cannot be treated conveniently within the usual framework of pss theory, since one assumes implicitly that the basis functions behave nearly adiabatically. However, Thorson and Levy[1] have shown that a theory of ionisation from adiabatic bound states to the electronic continuum can be developed as an extension of the pss method. Within a first-order perturbation, or distorted-wave, approximation, they proved that the transition probabilities for ionisation can be calculated using the nonadiabatic coupling matrix elements between the bound electronic states, ϕ_n, and the Born-Oppenheimer (fixed-nuclei) continuum states, $\phi_\varepsilon(\vec{r};\vec{R})$. I shall give a very brief account of the theory of Thorson and Levy[1] in section E of chapter II.

If electron translation factors are ignored, the matrix elements for ionisation are just the couplings, $\vec{P}_{\varepsilon n}(R)$,

$$\vec{P}_{\varepsilon n}(R) = -i\hbar \langle\phi_\varepsilon|(\vec{\nabla}_R)_{\vec{r}}|\phi_n\rangle. \qquad \text{(I-19)}$$

When etf's are included in the bound state description, these couplings are replaced by $\underline{P}_{\varepsilon n}+\underline{A}_{\varepsilon n}$, just as for couplings between bound states.

The etf corrections are of critical importance, not only to the calculation of ionisation matrix elements, but also in more general slow collision problems; in particular, one needs a way of choosing the switching function in the interaction region. With this in mind, I want now to describe briefly the history of the problem.

C. History

1. Introduction

In common with so many other problems in molecular physics, the origins of slow collision theory may be traced to the famous paper by Born and Oppenheimer[14] on the quantum mechanics of molecules. Since the electron to nuclear mass ratio is much less than unity, Born and Oppenheimer pointed out that characteristic nuclear speeds in the bound states of a molecular system will be much lower than those of electrons; therefore, an adiabatic separation of electronic and nuclear motion should be a good approximation. Their approach was based on a perturbation expansion in powers of $(m/\mu)^{\frac{1}{4}}$, and they were very careful to limit their discussion to non-degenerate, molecular states, in which the nuclear motion is bound; hence, the problem of asymptotic boundary conditions never arose. Nevertheless, it is very tempting to extend their idea directly to scattering problems, especially since the set of fixed-nuclei, electronic states is complete.[15]

A semiclassical treatment of slow collision problems, using the adiabatic basis states, was given by Mott[12] (essentially, equations (I-12) and (I-13)); the corresponding quantum mechanical version was developed by Mott and Massey[11] (equations (I-8) and (I-9)) and named the perturbed stationary states theory. In 1953, Bates, Massey and Stewart[16] published a detailed discussion of pss theory, applied to one-electron problems. As far as I know, this paper contains the first recognition that attempts to use pss theory for solving slow collision problems will run into fundamental difficulties. However, it wasn't until 1958 that Bates and McCarroll[3] showed that a correct theory must include some account of electron translation, at least asymptotically.

Since then, many different approaches to the problem have been tried. In 1976, Riera and Salin[17] wrote an excellent review of the subject, in which they analysed the various approaches and their defects, and pointed out the need for further work. Most of the proposed solutions, and all of them which correctly meet the boundary conditions, may be seen, in retrospect, as corresponding to different choices for the switching function. In the next subsection, I will discuss the various proposed solutions from this viewpoint. Of course, this is not the way that people actually thought about the problem, but it is convenient for linking the development of the subject to the present work. The final subsection covers the recent work by Thorson and Delos,[7] which goes a long way towards presenting a unified view of the theory of slow collisions.

2. Proposed Solutions to the ETF Problem

Many techniques have been proposed to avoid the difficulties encountered in the application of pss theory to practical problems. With one exception, these reduce to: (1) techniques which take f = constant; these are equivalent to using a single, <u>fixed</u> origin for electron co-ordinates, and (2) methods which correspond to particular switching functions. In the first category, f is <u>not</u> a switching function, as it <u>cannot</u> meet the asymptotic constraints, $f \to +1$ (-1) on B (A), for all states; only the methods in the second category are capable of meeting all boundary conditions.

a. <u>Methods Using a Fixed Reference Origin</u>

i. $f = -\lambda$. For completeness, we start with unmodified pss theory, which is recovered if we take $f = -\lambda$ (and drop the term in $(1-\lambda^2)$ in equation (I-16), which is just a phase). Thorson and Delos[7a] point out that pss theory may give reasonably good answers for certain types of problems. In degeneracy mediated processes, for example, $\vec{P}_{jn}(R)$ may be very large in the region of near-degeneracy (cf. equation (I-15)), while $\vec{A}_{jn}(R)$ is much smaller, and it may be an adequate approximation to ignore $\underline{\vec{A}}(R)$ altogether.

ii. $f = 0$. This has the effect of making the geometric centre (halfway between A and B) the origin of electron co-ordinates, and Riley,[9] and Schmid[18] have pointed out that such a correction may often be useful. It removes the spurious effects of nuclear mass asymmetry from pss theory, but does not remove the remaining errors, due to electron translation with respect to the geometric centre.

iii. f = +1. This choice makes nucleus B the reference origin for electron co-ordinates. The asymptotic wavefunctions describing electronic states bound to B are then exact, but those associated with A remain incorrect. Matrix elements linking two states on B have the correct asymptotic behaviour, but, as Riera and Salin[17] point out, there is no improvement for couplings involving states on A. This method can be used to calculate total charge exchange probabilities, but not individual transition cross sections. It has been used by Piacentini and Salin,[19] and, more recently, by Winter and Lane,[20] to treat charge exchange collisions in HeH^{++}.

iv. Scheme of Melius and Goddard.[21] These authors attempt to correct for etf effects by taking an origin which is effectively a weighted average over a molecular electronic state distribution. While $\underline{\vec{P}}(R)$ will generally vanish asymptotically for electrically asymmetric systems, this method cannot yield a consistently correct theory, and it will certainly fail for symmetric systems, such as H_2^+. Riera and Salin[17] have given a detailed criticism of this scheme.

b. Asymptotic $\underline{\vec{A}}$ Approximation

Chen et al.[22] propose to correct the nonadiabatic couplings, by subtracting from $\underline{\vec{P}}(R)$ its asymptotic value, i.e., $\underline{\vec{A}}(R) = \underline{\vec{A}}(\infty) = -\underline{\vec{P}}(\infty)$. They state that this can be justified by a formalism similar to that of "renormalisation" in quantum electrodynamics; it does not correspond to any simple assumption about f. In some special cases, this may be a useful approximation, but it is not generally adequate, as is pointed out both by Thorson and Delos,[7a] and by Riera and Salin.[17] Many pss matrix elements are spuriously large at finite R-values, even though they vanish asymptotically, and, in such cases, this method offers no improvement over pss theory. The ionising transitions provide a good example of the failure of this method.

The rest of this subsection deals with methods in category (2) described above, those which satisfy all asymptotic boundary conditions.

c. Asymptotic f Approximation

This is the method introduced by Bates and McCarroll.[3] Equivalent schemes, expressed in a variety of formalisms, have been developed by several other writers, notably Hahn[23] and Matveyenko.[24] This method assigns $f = +1$ for any state which is asymptotically associated with nucleus B, and $f = -1$ for states associated with A. For asymmetric systems, a unique, one-to-one correlation exists between molecular states and asymptotic atomic states; in symmetric systems, however, the correlation is not one-to-one. Bates and McCarroll[3] proposed a modification to handle this case, but it leads to complicated non-orthogonalities in the basis states, and to spurious couplings between states of g and u symmetry.

Even for asymmetric systems, at finite R, this approach does not give a very satisfactory description of states which are genuinely "molecular" in character. I will compare the results obtained using this approximation with those from the more sophisticated switching functions reported in this thesis. For HeH^{++}, the asymptotic f approximation is very good in some cases, but poor in others; it has been widely used in actual calculations.

d. Molecular Switching Function--Single f

In order to accomodate the molecular character of an electron in a slow collision, Schneiderman and Russek[6] introduced the idea of a switching function. If the electron is near A, $f = -1$; and, if it is near B, $f = +1$. To maintain orthogonality, they used a single switching function for all electronic states. This device takes care of the asymptotic behaviour, and also produces a realistic correction in the interaction region. The only problem is how to choose f, and different authors have used different forms, with varying success.

i. Schneiderman and Russek[6]

$$f = \cos\theta/\{1 + (\alpha/R)^2\},\ \alpha \text{ variable} \qquad \text{(I-20)}$$

ii. Mittleman and Tai[25]

$$f = (1-S^2)\ \{1-\exp(-2a\eta)\}/\{(1+S^2)\ [1+\exp(-2a\eta)] - 4\ S\ \exp(-a\eta)\}, \qquad \text{(I-21a)}$$

where

$$S = \{1 + aR + (aR)^2/3\}\ \exp(-aR), \qquad \text{(I-21b)}$$

$$a = 27/17, \qquad \eta = (r_A - r_B)/R. \qquad \text{(I-21c)}$$

iii. Taulbjerg et al.[26]

$$f = (\eta/2)\ (3-\eta^2)/\{1 + (\alpha/R)^2\},\ \alpha \text{ variable} \qquad \text{(I-22)}$$

iv. Levy and Thorson[1]

$$f = (r_A{}^2 - r_B{}^2)/(r_A{}^2 + r_B{}^2) \qquad \text{(I-23)}$$

f. <u>Molecular Switching Functions--state-dependent f's</u>

If we are prepared to push the physical interpretation of the switching function a little further, then we may expect f to be dependent on the bound state with which it is associated. As I pointed out earlier, for ionising transitions, the pss matrix elements are very large and very numerous; the corrected couplings are also very sensitive to the choice of f, and this was one of the reasons for the studies of switching functions made by Thorson and coworkers.[1,2]

For H_2^+, Thorson and Levy[1b] introduced the form

$$f = \tanh\{\beta(R)\ R\ \eta\}, \qquad \text{(I-24)}$$

where $\beta(R)$ is to be chosen for each initial bound state. Of course, if we use state-dependent f's, the electronic basis is once again non-orthogonal. In practice, this idea was remarkably successful: they found[2] that it was possible to choose $\beta(R)$ such that the number, size, and range of couplings are all drastically reduced. Couplings to all but the first two or three continuum partial waves are eliminated, and the spurious long-range behaviour of the remaining couplings is cancelled (the residual couplings have a range of about 10 au.). The corrected matrix elements to the higher partial waves are often as much as <u>four orders of magnitude smaller</u> than the corresponding pss values.

The calculations which form the core of this thesis confirm these results and extend them to other bound states of H_2^+, and to systems in which the nuclear charges are unequal, in particular, to HeH^{++}. After experimenting with various f's, I found that the most suitable one was

$$f = \tanh\{R[(\beta/2)\{(Z_A+Z_B)\eta+(Z_A-Z_B)\} + \alpha \ln(Z_B/Z_A)]\}, \qquad \text{(I-25)}$$

where α and β are variable parameters. The method used to select the parameters, α and β, is more systematic than that used by Thorson et al.,[2] but the same spectacular reductions are observed. The parameters which achieve this are independent of the continuum state properties and of the type of coupling involved (radial or angular), but <u>do</u> appear to be characteristic of the initial bound state. This behaviour is illustrated exhaustively in the thesis, and establishes beyond any reasonable doubt that the switching function approach to the problem of electron translation factors has a sound physical basis.

Since the switching functions determined here are, in some sense, characteristic of their corresponding bound states, it is reasonable to propose their use, not only in ionisation calculations, but also in more general, close-coupling problems. I shall discuss this proposal at some length in the final chapter of the thesis.

3. Formal Considerations

One difficulty with the whole subject of translation factor corrections has been the lack of a rigorous and fully quantum mechanical formulation; most discussions have used semiclassical or impact parameter treatments only. Recently, however, Thorson and Delos[7] have presented a formulation which runs parallel to pss theory, remedies all its defects, and establishes the correct form for the coupled equations to replace (I-9). They obtained the same results by two independent derivations, both of which use a single, molecular switching function. The first method[7a] introduces an etf explicitly, and uses a quantum mechanical transcription formula to eliminate the heavy particle velocity. The second derivation[7b] develops an idea originally proposed by Mittleman:[27] the switching function is used to define a non-linear co-ordinate transformation from molecular co-ordinates, $(\vec{r},\vec{R})$, to new co-ordinates, $(\vec{r},\vec{\xi})$, and the etf corrections are generated in the transformed Hamiltonian. In effect, this approach returns to the original idea of Born and Oppenheimer;[14] the new "scattering co-ordinate," $\vec{\xi}$, is defined in just such a way that the internal electronic motion is properly separated from the translational motion of the electron and nuclei, and a separate etf is not needed.

Some aspects of the problem remain unresolved. Other than the asymptotic constraints, the formulation of Thorson and Delos[7] gives no criteria for specifying the switching function. Formally, this presents no difficulty; provided one uses a complete set of electronic states, the solution to a scattering problem must be independent of the choice of f. However, in practice, the choice of f may have a significant effect on the behaviour of $\underline{\vec{P}}(R) + \underline{\vec{A}}(R)$, as the results presented in this thesis show. It is not known whether or not it is possible to give a unique, or "optimum," definition of either f or of the matrix, $\underline{A}(R)$, at finite R-values. Since a real calculation must use a severely truncated basis, an effective scheme for choosing f is of considerable practical, as well as formal, importance.

Using the classical trajectory approximation, Riley and Green[28] have used the Euler-Lagrange method to obtain equations which should, in principle, determine the form of electron translation factors, and, hence, f. However, these equations are very complicated, and, so far, they have only been solved for cases where f does not depend on the electron position.

In this thesis, I have taken an empirical approach to the determination of f: we have found, by calculation, that it is possible to choose an f for each bound state, which makes a large number of couplings from that state to the continuum very small. We think that the existence of these "optimum" f's is an interesting result, and, possibly, also a significant one. Since these f's are state-dependent, the results are not strictly compatible with the formulation given by Thorson and Delos.[7] However, the derivation can be extended to include the case of different f's for different states, at least in the classical trajectory limit; this will be covered in the Appendix.

D. Reader's Guide

In the next chapter, the basic theory of electron translation factors is described in detail. After he has read and digested this chapter, the reader is advised to return to chapter I and re-read section B; it should make a lot more sense the second time around. Chapter II is followed by two highly technical chapters, dealing with the computation of wavefunctions (III), and matrix elements (IV). On a first reading of chapter III, the reader should probably look at sections A, B-1, and C-1 only, which will provide useful background, without too much detail.

Chapter IV is a different matter. Sections A, B, and F summarise the first three chapters and set the scene for the results. I am very much afraid that sections C, D, and E will defeat all but the most dedicated reader, since they deal in great detail with the computation of individual matrix elements, and hence consist mostly of algebra. They provide a recipe for anyone wishing to carry out similar calculations, but should be read (if at all) only when the reader feels he has understood the rest of the thesis.

The results of my work are presented in chapter V. The way in which the switching functions were chosen is described, and some pictures of these "optimum" f's are given. These are followed by some two-dozen pictures of the resulting "optimised" matrix elements. It is ultimately these pictures which provide the justification for the etf approach to slow collision theory. The systematic cancellation of the pss matrix elements by several orders of magnitude is not fortuitous. In the final section of this chapter, some of the implications of these results are discussed.

CHAPTER II

THEORY

A. Co-ordinates

Consider a system composed of three particles, with masses, m_i, i = 1, 2, 3; and co-ordinates, $\vec{R}_i^{\,0}$, with respect to an external origin, and $\vec{r}_i$, with respect to the centre of mass of the system. Some other co-ordinates will also be useful (see figure 1).

i. Definition of the centre of mass:

$$\Sigma_i \, m_i \, \vec{r}_i = 0. \qquad \text{(II-1)}$$

ii. Centre of mass, $\vec{R}_{CM}^{\,0}$:

$$\vec{R}_{CM}^{\,0} = \Sigma_i \, m_i \, \vec{R}_i^{\,0}/m_T, \qquad \text{(II-2)}$$

$$\vec{r}_i = \vec{R}_i^{\,0} - \vec{R}_{CM}^{\,0}, \qquad m_T = \Sigma_i \, m_i. \qquad \text{(II-3)}$$

iii. Centre of mass of A and B, $\vec{R}_{AB}^{\,0}$:

$$\vec{R}_{AB}^{\,0} = (m_1\vec{R}_1^{\,0} + m_2\vec{R}_2^{\,0})/(m_1+m_2). \qquad \text{(II-4)}$$

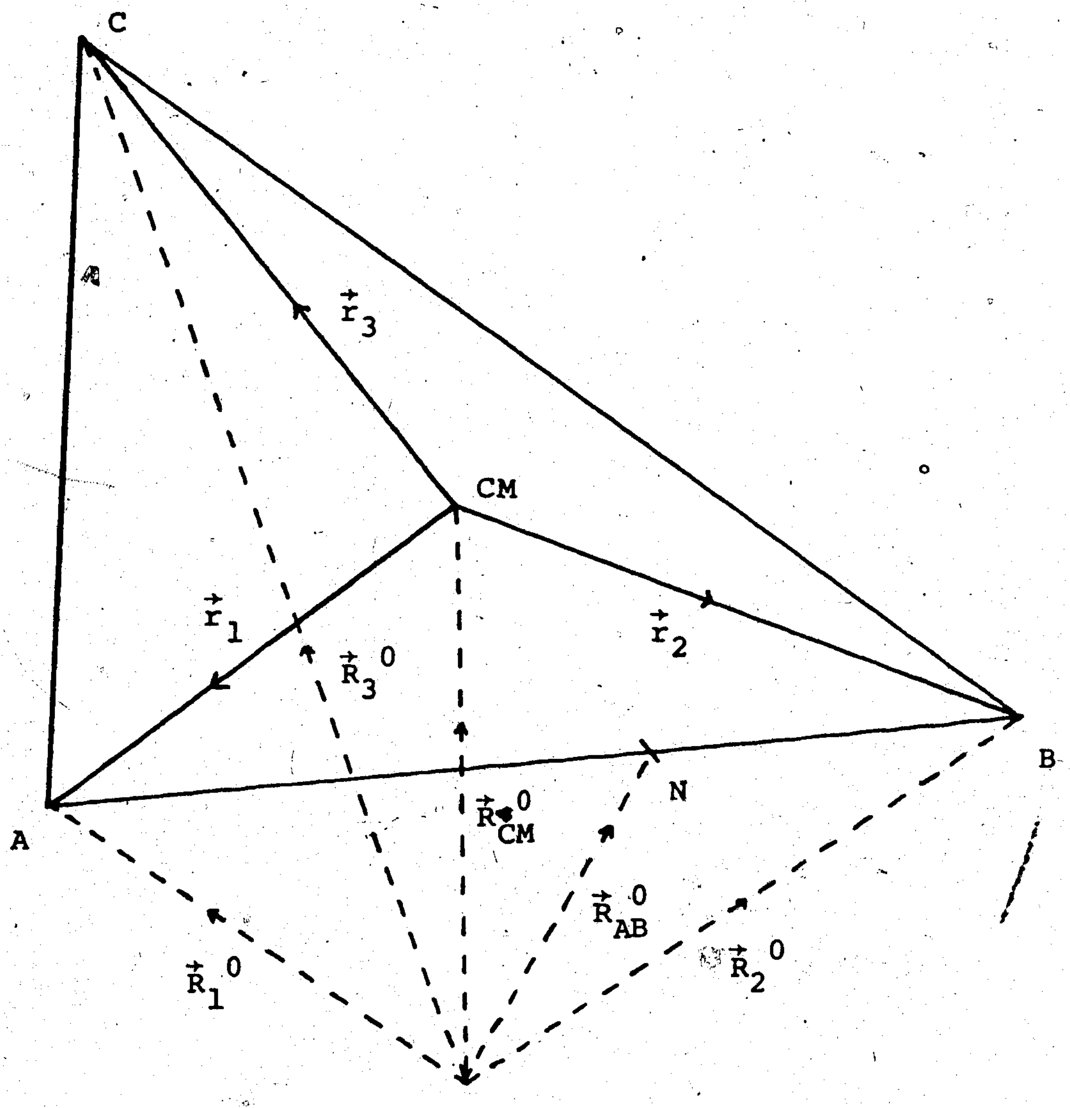

Figure 1. System Co-ordinates

iv. Relative co-ordinates, $\vec{q}_1$, $\vec{q}_2$:

$$\vec{q}_1 = \vec{r}_2 - \vec{r}_1, \tag{II-5a}$$

$$\vec{q}_2 = \vec{r}_3 - (m_1\vec{r}_1 + m_2\vec{r}_2)/(m_1+m_2). \tag{II-5b}$$

It is well known that we can write the total kinetic energy of the system as

$$T = T_{CM} + T', \tag{II-6a}$$

where

$$T_{CM} = \tfrac{1}{2}\, m_T(\dot{\vec{R}}{}^0_{CM})^2, \tag{II-6b}$$

$$T' = \tfrac{1}{2}\, \mu_1(\dot{\vec{q}}_1)^2 + \tfrac{1}{2}\, \mu_2(\dot{\vec{q}}_2)^2, \tag{II-6c}$$

$$\mu_1 = m_1m_2/(m_1+m_2), \qquad \mu_2 = m_3(m_1+m_2)/m_T. \tag{II-6d}$$

We can therefore factor out the centre of mass motion and write

$$\Psi_T = \Psi(\vec{q}_1,\vec{q}_2)\ \exp(i\vec{K}{}^0_{CM}\cdot\vec{R}{}^0_{CM}). \tag{II-7}$$

The internal motion is described by the co-ordinates, $\vec{q}_1$, the vector joining two of the particles; and $\vec{q}_2$, the position vector of the third particle, measured from the centre of mass of the other two.

Clearly, there are three ways in which these co-ordinates can be chosen. For systems composed of two heavy particles, masses M_A, M_B, and an electron, mass m_0, they are called the "molecular," "A-atom," and "B-atom" co-ordinates. These are illustrated in figure 2.

i. Molecular co-ordinates, $\vec{R}$, $\vec{r}$ (figure 2a):

$$\vec{q}_1 = \vec{R}, \qquad \vec{q}_2 = \vec{r}; \tag{II-8a}$$

$$\mu = M_A M_B/(M_A+M_B), \qquad m = m_0(M_A+M_B)/M_T; \tag{II-8b}$$

$$M_T = M_A + M_B + m_0, \qquad \lambda = (M_A-M_B)/(M_A+M_B). \tag{II-9}$$

λ is called the mass asymmetry parameter. It is also useful to define $\vec{r}_g$, the position vector of the electron, measured from the geometric centre (halfway between A and B):

$$\vec{r}_g = r - \tfrac{1}{2}\lambda\vec{R}. \tag{II-10}$$

ii. A-atom co-ordinates, $\vec{R}_A$, $\vec{r}_A$ (figure 2b):

$$\vec{q}_2 = \vec{R}_A = \{M_A M_T/(M_A+M_B)\}\vec{R} - \{m_0/(M_A+m_0)\}\vec{r}, \tag{II-11a}$$

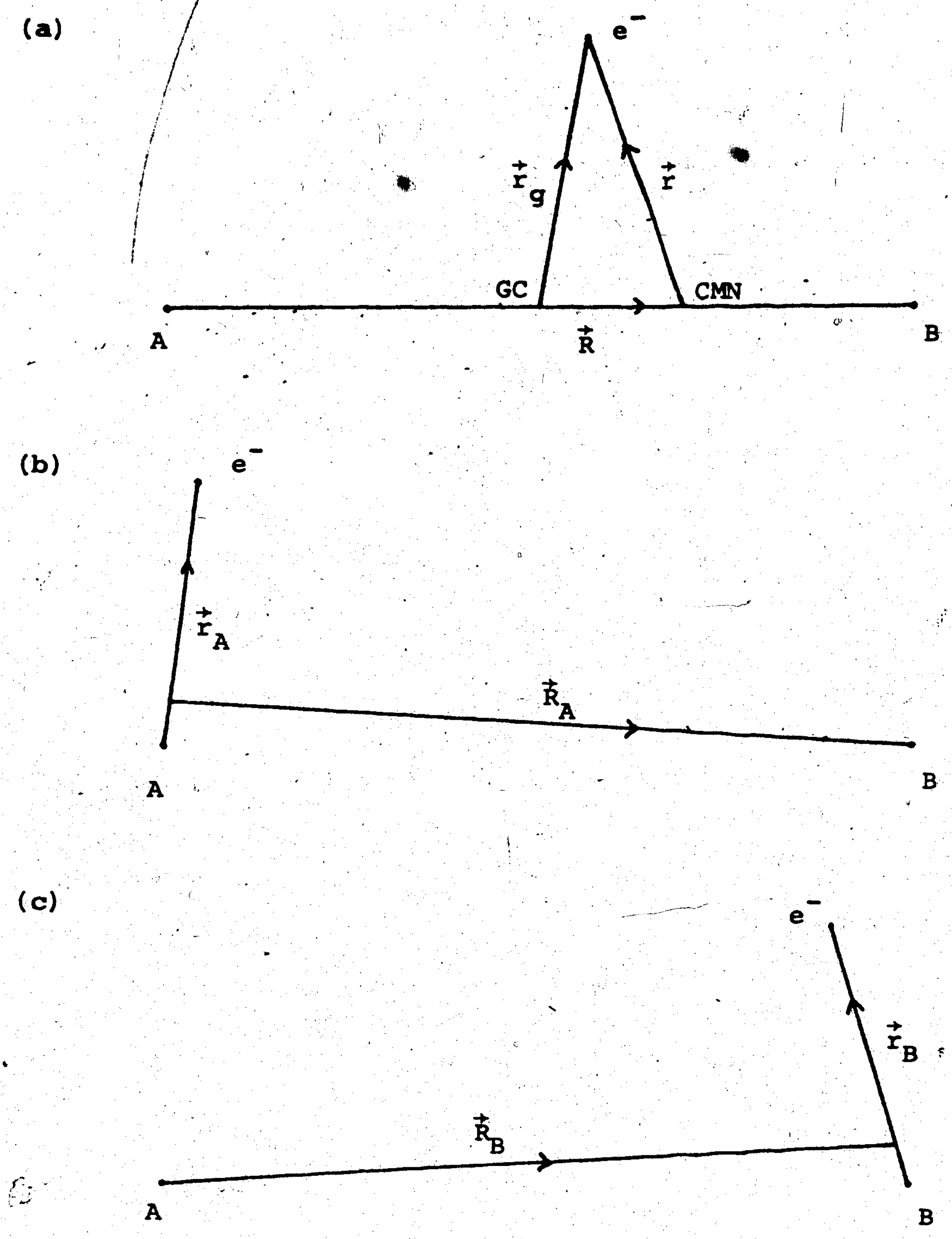

Figure 2. Jacobi Co-ordinates

$$\vec{q}_1 = \vec{r}_A = \vec{r} - \tfrac{1}{2}\,(\lambda-1)\;\vec{R}; \qquad \text{(II-11b)}$$

$$\mu_A = M_B(M_A+m_0)/M_T, \qquad m_A = M_A m_0/(M_A+m_0). \qquad \text{(II-12)}$$

iii. B-atom co-ordinates, $\vec{R}_B$, $\vec{r}_B$ (figure 2c):

$$\vec{q}_2 = \vec{R}_B = \{M_B M_T/(M_A+M_B)\}\vec{R} + \{m_0/(M_B+m_0)\}\vec{r}, \qquad \text{(II-13a)}$$

$$\vec{q}_1 = \vec{r}_B = \vec{r} - \tfrac{1}{2}\,(\lambda+1)\;\vec{R}; \qquad \text{(II-13b)}$$

$$\mu_B = M_A(M_B+m_0)/M_T, \qquad m_B = M_B m_0/(M_B+m_0). \qquad \text{(II-14)}$$

I want now to introduce a function, f_J, where J is A or B, defined such that $f_B = +1$, and $f_A = -1$. With this device, we can use a single form to express both sets of atomic co-ordinates, in terms of molecular co-ordinates.

$$\vec{R}_J = (\mu/\mu_J)\;\{\vec{R} + (m/2\mu)(f_J+\lambda)\;\vec{r}\}, \qquad \text{(II-15a)}$$

$$\vec{r}_J = \vec{r} - \tfrac{1}{2}\,(f_J+\lambda)\;\vec{R}; \qquad \text{(II-15b)}$$

$$\mu_J/\mu = \{1 + (m_0/2\mu)(1+f_J\lambda)\}\;(M_A+M_B)/M_T, \qquad \text{(II-16a)}$$

$$m_0/m_J = 1 + (m_0/2\mu)(1+f_J\lambda). \qquad \text{(II-16b)}$$

Equations (II-15) and (II-16) are needed for the next section, in which I examine the boundary conditions on Ψ and show why the pss theory gives a poor description of collision processes. Two other equations will also be useful:

$$M_T/(M_A+M_B) = 1 + \tfrac{1}{2}\,(1-\lambda^2)\; m_0/\mu, \qquad \text{(II-17a)}$$

$$M_A M_B/M_T = \mu(M_A+M_B)/M_T = \tilde{\mu}. \qquad \text{(II-17b)}$$

B. Asymptotic Boundary Conditions and Translation Factors

1. Origin of the Translation Factor[7a]

Suppose that asymptotically the electron is in the atomic state, $\phi^0_{n_J}$, on atom J, with energy, ε_{n_J}. Then the asymptotic solution to the time-independent Schrödinger equation is

$$\Psi \sim \phi^0_{n_J}(\vec{r}_J)\, \exp(i\vec{k}_J.\vec{R}_J), \qquad \text{(II-18)}$$

where

$$h^2 k_J^{\,2} = 2\mu_J(E-\varepsilon_{n_J}). \qquad \text{(II-19)}$$

We now transform the plane wave factor to molecular coordinates, using equation (II-15a). However, this must be done carefully, since the appearance of the atomic reduced mass, μ_J, in equation (II-19) means that the wave-vector,

$\vec{k}_J$, is an intrinsic function of the atomic configuration. (The extrinsic dependence on ε_{n_J} is not important.) This configuration dependence can be eliminated by defining a molecular wave-vector, $\vec{k}$, such that

$$\vec{k}_J = (\mu_J/\mu)^{\frac{1}{2}} \vec{k}; \tag{II-20}$$

and this implies that

$$\vec{k}_J.\vec{R}_J = (\mu/\mu_J)^{\frac{1}{2}} \vec{k}.\{\vec{R} + (m/2\mu)(f_J+\lambda)\ \vec{r}\}. \tag{II-21}$$

But $(m/\mu) << 1$, so we expand (μ/μ_J) in powers of (m/μ), and keep only the lowest terms. From equations (II-16a) and (II-17a), it can be seen that

$$(\mu/\mu_J)^{\frac{1}{2}} \simeq 1 - (m_0/8\mu)\ (1+2f_J\lambda+\lambda^2), \tag{II-22}$$

and

$$\vec{k}_J.\vec{R}_J \simeq \vec{k}.\{\vec{R} + (m/\mu)\ \vec{s}\}, \tag{II-23}$$

where

$$\vec{s} = \tfrac{1}{2}\ (f_J+\lambda)\ \vec{r}_g - (1-\lambda^2)\ \vec{R}/8. \tag{II-24}$$

The term, $\exp[(im/\mu)\vec{k}.\vec{s}]$, which thus appears in equation (II-18), is called the electron translation factor; and, if we define a classical heavy-particle velocity, $\vec{v} = \hbar\vec{k}/\mu$, it can be given a simple physical interpretation. $(f_J+\lambda)\vec{v}/2$ is just the translational velocity of the electron, with respect to the centre of mass of the nuclei, due to the motion of the nucleus to which it is bound; and the remaining term represents the electron transport kinetic energy, due to the nuclear motion. Noting that $f_J{}^2 = 1$, for a straight-line trajectory $\vec{R} = \vec{b} + \vec{v}t$ ($\vec{b}$ is called the impact parameter), we can re-write equation (II-23) as

$$\vec{k}_J.\vec{R}_J \simeq \vec{k}.\vec{R} + (m/\hbar)\ (\vec{w}.\vec{r} - w^2t/2), \qquad \text{(II-25a)}$$

where

$$\vec{w} = (f_J+\lambda)\vec{v}/2. \qquad \text{(II-25b)}$$

Part of the kinetic energy is independent of the system configuration (i.e., of f_J), and it is convenient to isolate this term:

$$\vec{k}_J.\vec{R}_J \simeq \vec{k}.[\vec{R}+(m/\mu)\vec{s}\,'] - (m/\hbar)(1-\lambda^2)v^2t/8, \qquad \text{(II-26a)}$$

where

$$\vec{s}' = \tfrac{1}{2}\,(f_J+\lambda)\,\vec{r}_g. \tag{II-26b}$$

Alternatively, we could absorb the final term into the definition of the molecular wave-vector. If we take

$$\vec{k}_J = (\mu_J/\tilde{\mu})^{\frac{1}{2}}\,\vec{k}', \tag{II-27a}$$

where $\tilde{\mu}$ is defined in equation (II-17b), and notice that

$$m_0/\mu = m/\tilde{\mu}, \tag{II-27b}$$

then it is easy to see that

$$\vec{k}_J.\vec{R}_J \simeq \vec{k}'.[\vec{R} + (m/\tilde{\mu})\vec{s}\,']. \tag{II-28}$$

2. Defects of PSS Theory

a. Introduction

I want now to examine the pss theory in the light of this study of the boundary conditions. As the reader will recall, in the pss method, the wavefunction is expanded in terms of the Born-Oppenheimer, molecular eigenfunctions (equation (I-8)):[11]

$$\Psi(\vec{r},\vec{R}) = \Sigma_n \chi_n(\vec{R})\ \phi_n(\vec{r};\vec{R}), \tag{II-29}$$

and the resulting equations, (I-9), are coupled by the matrix, $\underline{\vec{P}}(R)$, where

$$\vec{P}_{jn}(R) = -i\hbar \langle\phi_j|(\vec{\nabla}_R)_{\vec{r}}|\phi_n\rangle. \qquad \text{(II-30)}$$

In pss theory, individual terms in the expansion, (II-29), are interpreted asymptotically as scattering wavefunctions for electronic states, ϕ_n^{∞} [i.e., the states $\phi_n(\vec{r};\vec{R},R\to\infty)$], and these states are presumed to correspond in some simple way to the exact atomic states, $\phi_{n_J}^{0}$. For simplicity, let us first consider electrically asymmetric systems, in which this correspondence is one-to-one. If one can express the exact plane-wave state, (II-18), as a single product, $\phi_n^{\infty}\chi_n(\vec{R})$, then, and only then, one can interpret this product as a scattering wavefunction for the atomic state, $\phi_{n_J}^{0}$.

However, it is immediately obvious that <u>no electron translation factor appears</u> in the product $\phi_n^{\infty}\chi_n(\vec{R})$. For our purposes, this is the important problem, but there is another, minor error, related to the fact that ϕ_n^{∞} is not <u>exactly</u> equal to $\phi_{n_J}^{0}$; for completeness, we will dispose of this latter defect first.

b. <u>Asymptotic Electronic States</u>

The exact atomic states are eigenfunctions of a Hamiltonian, h_{at}^{J}, which uses the <u>atomic</u> electron reduced mass, m_J, whereas the <u>molecular</u> reduced mass, m, appears in the Hamiltonian, h_e. Thus, asymptotically,

$$h_{at}^{J} = h_e - (\hbar^2/2)\,(m_J^{-1} - m^{-1})\,(\nabla_r^{\,2})_{\vec{R}}; \qquad \text{(II-31)}$$

and the final term can be treated as a small perturbation, as it is of order (m/μ) times the electron kinetic energy. It then follows that the atomic eigenvalue, ϵ_{n_J}, is given, correct to first order, by

$$\epsilon_{n_J} \simeq \lim_{R\to\infty} \{\epsilon_n(R) - (\hbar^2/2)(m_J^{-1}-m^{-1})\langle\phi_n|(\nabla_r^{\,2})_{\vec{R}}|\phi_n\rangle\}, \qquad \text{(II-32a)}$$

where ϕ_n tends to the approximate atomic state, ϕ_n^{∞}. Using equations (II-15) and (16), we can rewrite the second term, so that

$$\epsilon_{n_J} \simeq \lim_{R\to\infty} \{\epsilon_n(R) - (\hbar^2/2\mu)\langle\phi_n|(\nabla_R^{\,2})_{\vec{r}}|\phi_n\rangle\}. \qquad \text{(II-32b)}$$

As equation (I-11) shows, this correction <u>does</u> appear in the pss coupled equations, (I-9), a fact which is well-known;[29-31] as one might expect, it does not appear in the classical trajectory equations, (I-13). Unless one is interested in isotope splitting effects, these corrections to the atomic binding energies are unimportant; I propose to ignore them and assume that the molecular states provide an adequate asymptotic description of the limiting atomic states. In their rigorous formulation, Thorson and Delos[7b] treat this point much more carefully, and show that the corrected theory also recovers the correct binding energies, to the required accuracy in (m/μ).

In electrically symmetric systems, the Born-Oppenheimer wavefunctions occur in asymptotically degenerate, (g, u) pairs. However, limiting atomic states can be constructed as linear combinations of the g and u molecular states,

$$\phi_{n_J} = \lim_{R\to\infty} 2^{-\frac{1}{2}} \{\phi_n{}^g(\vec{r};\vec{R}) + f_J\, \phi_n{}^u(\vec{r};\vec{R})\}, \qquad \text{(II-33)}$$

after which, the discus[illegible]on proceeds as before.

c. Translation Factors [illegible] PSS Theory

Let us now turn [illegible]ttention to the really important defect of pss theory. Suppose that the electron is asymptotically in state ϕ_{n_J}, where

$$\phi_n(\vec{r};\vec{R}) \sim \phi_{n_J}(\vec{r}_J), \text{ as } R\to\infty. \qquad \text{(II-34)}$$

An asymptotic solution to the pss equations (I-9) may be written

$$\Psi \sim \phi_{n_J} \exp(i\vec{k}.\vec{R}), \qquad \text{(II-35)}$$

where

$$\hbar^2 k^2 = 2\mu[E-\varepsilon_n(\infty)]; \qquad \text{(II-36)}$$

and, in pss theory, this is assumed to be equivalent to (II-18). However, from (II-26), or (II-28), it can be seen that no translation factor appears, and hence, Ψ as defined by (II-35) is <u>not</u> equivalent to (II-18). Only by using a complete expansion (including the electronic continuum), can one make the form, (II-29), represent a solution like (II-18); such an expansion is clearly impractical. Since individual terms in the pss expansion do not represent real, physical states, it is not surprising that the couplings between them show unphysical behaviour.

To show how the spurious asymptotic coupling arises, let us examine the nonadiabatic coupling matrix, $\underline{\vec{P}}(R)$, in detail. $\underline{\vec{P}}(R)$ is the matrix of the operator, $-i\hbar(\vec{\nabla}_R)_{\vec{r}}$, in the space of the Born-Oppenheimer functions, and it is evaluated holding the electron fixed, with respect to the centre of mass of the nuclei. From (II-15b), it can be seen that

$$-i\hbar(\vec{\nabla}_R)_{\vec{r}} = -i\hbar\,[(\vec{\nabla}_R)_{\vec{r}_J} - \tfrac{1}{2}\,(f_J+\lambda)\,(\vec{\nabla}_{r_J})_{\vec{R}}]. \quad \text{(II-37)}$$

Asymptotically, the contribution to $\underline{\vec{P}}(R)$ arising from the first term in equation (II-37) represents deformation of the adiabatic wavefunctions, as $\vec{R}$ changes, and it must vanish, since, according to equation (II-34), the $\phi_n(\vec{r};\vec{R})$ become functions only of $\vec{r}_J$. However, some states asymptotically associated with the same centre will be connected by the momentum operator, $-i\hbar(\vec{\nabla}_{r_J})_{\vec{R}}$, and, for such states, $\vec{P}_{jn}(R)$ will tend to a constant, as $R\to\infty$. This term represents the displacement of a wavefunction, without deformation, and it is entirely spurious. The physically-appropriate reference origin is atom J, not the CMN. At finite R-values, it is not possible to decompose $\underline{\vec{P}}(R)$ uniquely into deformation terms plus displacement effects, but it is clear nevertheless, that the latter are often large, and that they have no place in the theory.

3. Modified Electronic Basis

From the above discussion, it is clear that we can avoid the defects of pss theory by including an account of electron translation in the electronic basis. In the classical trajectory approximation, we can do this simply by replacing the Born-Oppenheimer basis with the modified states,

$$\Phi_n\{\vec{r};\vec{R}(t)\} = \phi_n\{\vec{r};\vec{R}(t)\}\ F_n, \tag{II-38}$$

where F_n is an electron translation factor, defined by

$$F_n = \exp\{(im/\hbar)\ \vec{v}.\vec{s}_n\}. \tag{II-39}$$

The exponent, $\vec{s}_n$, must tend to the correct asymptotic value, given by equation (II-24), but it should also reflect the fact that the electron is <u>molecular</u> for much of the collision, with appreciable density near both nuclei. For this reason, we introduce a molecular switching function, $f(\vec{r};\vec{R})$,[6] defined such that

$$\lim_{R\to\infty} f(\vec{r};\vec{R}) = f_J,\ r_J \text{ finite}; \qquad \text{(II-40a)}$$

$$\lim_{r\to\infty} f(\vec{r};\vec{R}) = 0,\ R \text{ finite}; \qquad \text{(II-40b)}$$

$$f(-\vec{r};\vec{R}) = -f(\vec{r};\vec{R}),\ \text{if } Z_A = Z_B; \qquad \text{(II-40c)}$$

but f is otherwise unconstrained. We will thus obtain a suitable etf by defining $\vec{s}_n$, such that

$$\vec{v}.\vec{s}_n = \vec{v}.\vec{s} - \int^t (1-\lambda^2) v^2 dt'/8, \qquad \text{(II-41a)}$$

$$\vec{s} = \tfrac{1}{2}(f+\lambda)\,\vec{r}_g. \qquad \text{(II-41b)}$$

Note that the $\vec{s}$ of equations (II-41) tends asymptotically, to the $\vec{s}'$ of equation (II-28). In equation (II-38), I have allowed for different F_n's for different states; this flexibility would be provided by choosing distinct f_n's in the definition of $\vec{s}$. However, for the moment, I shall take the simpler case of a single, common f, and generalise the results obtained later.

From the point of view of a fully quantum mechanical theory, the modified basis is still defective, since the classical nuclear velocity appears in the translation factor. In their first formulation, Thorson and Delos[7a] introduce an ad hoc, quantum mechanical transcription to eliminate $\vec{v}$; their second derivation,[7b] based on a coordinate transformation, gives the same final result and justifies the transcription. Here, I shall use a classical trajectory approach, which is much simpler, but still retains all the essential features.

C. Classical Trajectory Equations

In this section, I will derive the appropriate coupled equations to replace equations (I-13), using a basis of Born-Oppenheimer adiabatic states, modified by a translation factor. We assume that the nuclei follow a specified classical path, $\vec{R}(t)$, with velocity $\vec{v} = d\vec{R}/dt$, and write the solution to the time-dependent Schrödinger equation as

$$T = \Sigma_n \; a_n(t) \; \Phi_n(\vec{r};\vec{R}) \; \exp\{-i\int^t \varepsilon_n(t')dt'/\hbar\}, \qquad \text{(II-42)}$$

where $\Phi_n(\vec{r};\vec{R})$ is defined by equations (II-38) to (II-41). This implies the system of coupled equations

$$i\hbar \; \dot{\underline{b}} = [\underline{h} + \vec{v}.\underline{\vec{D}}] \; \underline{b}, \qquad \text{(II-43)}$$

where

$$b_n = a_n \exp\{-i\int^t \varepsilon_n(t')dt'/\hbar\}, \tag{II-44}$$

$$h_{jn} = \langle\phi_j|h_e|\phi_n\rangle, \tag{II-45}$$

$$\vec{D}_{jn} = -i\hbar \langle\phi_j|(\vec{\nabla}_R)_{\vec{r}}|\phi_n\rangle. \tag{II-46}$$

Now

$$h_{jn} = \varepsilon_n\delta_{jn} + \langle\phi_j|F^*[h_e,F]|\phi_n\rangle, \tag{II-47}$$

$$\vec{P}_{jn}(R) = -i\hbar \langle\phi_j|(\vec{\nabla}_R)_{\vec{r}}|\phi_n\rangle; \tag{II-48}$$

and the remaining term is thus

$$\langle\phi_j|F^*\{[h_e,F] - i\hbar\ \partial F/\partial t\}|\phi_n\rangle. \tag{II-49}$$

If we discard the terms in (II-49) involving $\partial\vec{v}/\partial t$, and those of order v^2, we find that

$$i\hbar\ \dot{\underline{b}} = [\underline{\varepsilon} + \vec{v}.(\underline{\vec{P}}+\underline{\vec{A}})]\ \underline{b} \tag{II-50a}$$

or

$$i\hbar\ \dot{a}_j = \Sigma_n\ \vec{v}.(\vec{P}_{jn}+\vec{A}_{jn})\ a_n(t) \exp\{-i\int^t(\varepsilon_n-\varepsilon_j)dt'/\hbar\}, \tag{II-50b}$$

where

$$A_{jn}(R) = (im/\hbar)\ \langle\phi_j|[h_e,s]|\phi_n\rangle. \qquad \text{(II-51)}$$

Equations (II-50) are the desired classical trajectory equations. The only difference between (II-50) and the pss equations, (I-13), is that the nonadiabatic coupling matrix, $\underline{\vec{P}}(R)$, has been replaced by $\underline{\vec{P}}(R)+\underline{\vec{A}}(R)$.

D. Effect of Translation Factor Corrections

From equation (II-51), it can be seen that

$$\vec{A}_{jn}(R) = (im/\hbar)\ (\varepsilon_j-\varepsilon_n)\ \langle\phi_j|\vec{s}|\phi_n\rangle \qquad \text{(II-52a)}$$

$$= -i\hbar\ \langle\phi_j|(\vec{\nabla}_r\vec{s})\cdot\vec{\nabla}_r + \tfrac{1}{2}\ (\nabla_r{}^2\vec{s})|\phi_n\rangle; \qquad \text{(II-52b)}$$

and the reader will recall that

$$\vec{s} = \tfrac{1}{2}\ (f+\lambda)\ \vec{r}_g. \qquad \text{(II-53)}$$

Therefore, as $R\to\infty$,

$$\vec{A}_{jn}(R) \sim \tfrac{1}{2}\ (f_J+\lambda)\ \langle\phi_{j_J}|(-i\hbar\vec{\nabla}_{r_J})|\phi_{n_J}\rangle. \qquad \text{(II-54a)}$$

But, from equation (II-37), we see that

$$\vec{P}_{jn}(R) \sim -\ \tfrac{1}{2}\ (f_J+\lambda)\ \langle\phi_{j_J}|(-i\hbar\vec{\nabla}_{r_J})|\phi_{n_J}\rangle. \qquad \text{(II-54b)}$$

Thus, $\underline{\vec{A}}(R)$ exactly cancels the spurious, infinite-range couplings contained in $\underline{\vec{P}}(R)$:

$$\lim_{R\to\infty} [\underline{\vec{P}}(R) + \underline{\vec{A}}(R)] = \underline{\vec{0}}. \tag{II-55}$$

Of course, that was the main reason for introducing the etf in the first place!

For systems with unequal nuclear masses, $\underline{\vec{P}}(R)$ contains a term proportional to λ, since the origin of electron co-ordinates is the centre of mass of the nuclei. However, nonadiabatic couplings are supposed to represent properties of the electronic wavefunctions and thus should be independent of λ. The additional term is fictitious, and it is exactly cancelled at all R by a corresponding term in $\underline{\vec{A}}(R)$. This is easily shown:

$$(-i\hbar\vec{\nabla}_R)_{\vec{r}} = (-i\hbar\vec{\nabla}_R)_{\vec{r}_g} - \tfrac{1}{2}\lambda\,(-i\hbar\vec{\nabla}_r)_{\vec{R}}, \tag{II-56a}$$

and

$$(im/\hbar)\,[h_e,\vec{s}] = (im/\hbar)\,[h_e,\vec{s}_g] + \tfrac{1}{2}\lambda(-i\hbar\vec{\nabla}_r)_{\vec{R}}, \tag{II-56b}$$

where

$$\vec{s}_g = \tfrac{1}{2}\, f\, \vec{r}_g. \tag{II-56c}$$

The second term in (II-56b) exactly cancels the second term in (II-56a), so we have the result that

$$\underline{\vec{P}}(R) + \underline{\vec{A}}(R) = \underline{\vec{P}}^g(R) + \underline{\vec{A}}^g(R), \qquad \text{(II-57a)}$$

where

$$\vec{P}^g_{jn}(R) = -i\hbar \langle\phi_j|(\vec{\nabla}_R)_{\vec{r}_g}|\phi_n\rangle, \qquad \text{(II-57b)}$$

and

$$\vec{A}^g_{jn}(R) = (im/\hbar) \langle\phi_j|[h_e,\vec{s}_g]|\phi_n\rangle. \qquad \text{(II-57c)}$$

How is $\underline{\vec{A}}(R)$ to be interpreted? At large R, we have seen that $\underline{\vec{P}}(R)$ can be separated into a distortion term, which tends to zero, and a displacement term. The latter is spurious, and it is exactly cancelled by $\underline{\vec{A}}(R)$. We may suppose that $\underline{\vec{A}}(R)$ plays much the same role at finite R-values: it identifies and removes that part of $\underline{\vec{P}}(R)$ which represents displacement without deformation, leaving only the distortion effects. However, since there is no obvious and unique way of isolating just the translation effects, $\underline{\vec{A}}(R)$ can only be defined uniquely in the asymptotic limit. This ambiguity is reflected in the fact that the theory gives no way of determining f in the interaction region. Formally, this does not matter: the set of

Born-Oppenheimer states is complete, and any "sensible" f which satisfies the boundary conditions will do.

In practice, the choice of f is important, since one must always work with a truncated basis, and, in many cases, the corrected matrix elements are very sensitive to the choice of f. In this work, I examine the way in which the corrected matrix elements for ionising transitions depend on the switching function. The behaviour of these matrix elements allows us to choose very clear-cut, "sensible" f's.

Two tasks are required to complete this chapter. In section E, I give a brief account of the theory of direct-impact ionisation in slow collisions, to provide a background for the examination of ionisation matrix elements. Finally, section F deals with the transformation of electron co-ordinates from a space-fixed reference frame, to a frame rotating with the molecular axis.

E. Ionisation in near-adiabatic Collisions

1. Introduction

As I pointed out in chapter I, ionising transitions cannot be handled within the close-coupled expansion scheme of pss theory (even if electron translation effects are included). The expansion uses a truncated basis of adiabatic states, and assumes that (in a slow collision) electrons in those states behave nearly adiabatically.

But, because of their high degeneracy, the continuum and Rydberg levels can never behave adiabatically, and to include them in a straightforward pss expansion would mean using an intractably large basis.

However, in direct impact processes, large changes in the electronic energy occur upon transition, and hence the probability of such transitions is small, at least in slow collisions. Thus, one may be able to treat ionisation from tightly bound electronic states by a perturbative approach, in which the perturbation causing transitions is the "deformation" of the initial-state wavefunction, projected onto the continuum states of the system. What is then needed is a description of these states, and a definition of the probabilities of transitions to them.

A first-order perturbation theory of direct impact ionisation in slow atomic collisions has been given by Thorson and Levy.[1a] It leads to a "distorted-wave" approximation for the ionisation cross sections, and the reader is referred to their long paper for a detailed discussion; here, I shall describe only the main physical ideas.

2. The "Fast Electron" Approximation

An adiabatic electron is one whose (bound) orbital speed is so much greater than the nuclear speed that it can adjust smoothly to changes in the nuclear position.

By contrast, a continuum electron has a classically aperiodic orbit, so that it cannot be said to follow the nuclear motion adiabatically. Nevertheless, the characteristic speed of a continuum electron will still, in general, be much greater than that of the nuclei. This means that an electron in an unbound orbit will move through the system and out to infinity in a time so short, that the nuclear configuration will hardly change at all, and the orbit will essentially be that of an electron in the "fixed-nuclei" system.

In the language of quantum mechanics, an electron instantaneously excited to a continuum state at time, t', will produce a signal at a detector at some later time, t; but the signal will reflect the nuclear configuration at the <u>excitation time</u>, $\vec{R}(t')$, and <u>not</u> that at the signal time, $\vec{R}(t)$. By taking a coherent sum of the instantaneous amplitudes at each point along a trajectory, $\vec{R}(t')$, one obtains the cumulative signal amplitude over an entire collision. The instantaneous amplitudes for the excitation of an electron to a continuum state with energy, ε, is the projection of the nonadiabatic perturbation of the initial state onto the Born-Oppenheimer continuum state; and the matrix element for this is just $\vec{P}_{\varepsilon n}$ (in pss theory), or $\vec{P}_{\varepsilon n} + \vec{A}_{\varepsilon n}$ (in the corrected theory). To give a correct description of the ionised electron, as it moves out to the detector, one must also include a transformation from the rotating molecular frame back to the laboratory frame, but the basic physical idea of the Thorson and Levy ionisation theory[1a] is that described above.

On either side of the ionisation threshold, there is a band of states in which the electron is neither "fast" nor "adiabatic." In these states, characteristic electron speeds are of the same order as, or less than, the nuclear speeds, and hence, for collisions involving ~~these states~~, the electron motion will be very complicated. Second order processes, such as ionisation followed by recapture, will be common, and no simple theory exists to deal with these "slow electron" levels. For slow collisions, the band of states is less than 0.5 eV wide, and transitions to such states are unlikely to contribute much to the overall cross section.[1a]

3. Ionising Transitions and Switching Functions

For the purposes of this thesis, the important conclusion to be drawn from the work of Thorson and Levy[1a] is that the matrix elements governing ionisation are $\vec{P}_{\varepsilon n}+\vec{A}_{\varepsilon n}$, between bound and continuum Born-Oppenheimer eigenfunctions.

In chapter I, I described the physically unrealistic behaviour of the uncorrected pss matrix elements. I also discussed how Thorson and coworkers[1b] found, for H_2^+, that it is possible to choose a switching function for each bound state, such that the size, number, and range of the couplings from that state to the continuum are all greatly reduced. In this thesis, I confirm and considerably extend these results, and also make them much more precise. If the f's so obtained can be called "best" choices, in some sense, then they could be said to provide an "optimum" way of isolating the (so far undefined) "deformation" part of $\vec{\underline{P}}(R)$.

Our method for choosing switching functions will be described at length in chapter V. Both the studies reported in this thesis and the earlier work of Thorson et al.[1b] indicate clearly that different f's are needed for different bound states; in chapter V, I shall also consider how to modify the theory to take account of this.

F. Rotating Frame Co-ordinates

Up to this point, I have assumed that the electronic states, $\phi_n(\vec{r};\vec{R})$, and Hamiltonian, h_e, are expressed in terms of electron co-ordinates, $\vec{r}$, in a reference frame whose axes are fixed in space; in particular, the gradient, $(\vec{\nabla}_R)_{\vec{r}}$, is evaluated with $\vec{r}$ fixed in this frame. However, as is well-known, the molecular electronic states and Born–Oppenheimer Hamiltonian are normally described in a rotating reference frame, whose polar axis coincides with $\vec{R}$; let us denote the electron co-ordinates in this frame by $\vec{r}'$. In the rotating frame, the transformed Hamiltonian, h_e', and wavefunctions, ϕ_n', depend upon $\vec{r}'$ and $R = |\vec{R}|$, but do not depend on the orientation of the vector, $\vec{R}$, in space.

The transformation linking the components, (x',y', z'), of $\vec{r}'$, to the components, (x,y,z), of $\vec{r}$, is[7a]

$$\begin{pmatrix} x' \\ y' \\ z' \end{pmatrix} = \begin{pmatrix} \cos\Theta\,\cos\Phi & \cos\Theta\,\sin\Phi & -\sin\Theta \\ -\sin\Phi & \cos\Phi & 0 \\ \sin\Theta\,\cos\Phi & \sin\Theta\,\sin\Phi & \cos\Theta \end{pmatrix} \begin{pmatrix} x \\ y \\ z \end{pmatrix} \qquad \text{(II-58)}$$

where $\vec{R}$ has polar co-ordinates, (R,Θ,Φ). Note that the y'-axis coincides with the line of nodes and is therefore perpendicular to the plane containing the z- and z'-axes.

Using equation (II-58), we can express the components of the gradient,

$$-i\hbar\,(\vec{\nabla}_R)_{\vec{r}}\,\phi_n(\vec{r};\vec{R})$$

in terms of operators in the rotating frame.[32-34] Noting that

$$\phi_n(\vec{r};\vec{R}) = \phi_n{}'(\vec{r}\,';R), \qquad \text{(II-59)}$$

a straightforward application of vector calculus yields the result that

$$-i\hbar\,[\partial\phi_n(\vec{r};\vec{R})/\partial R]_{\vec{r}} = -i\hbar\,[\partial\phi_n{}'(\vec{r}\,';R)/\partial R]_{\vec{r}\,'}, \qquad \text{(II-60a)}$$

$$-i\hbar\,[\partial\phi_n(\vec{r};\vec{R})/\partial\Theta]_r = -\hat{L}_{y'}\,\phi_n'(\vec{r}';R), \qquad \text{(II-60b)}$$

$$-i\hbar\,[\partial\phi_n(\vec{r};\vec{R})/\partial\Phi]_{\vec{r}} = \{\hat{L}_{x'}\sin\Theta - \hat{L}_{z'}\cos\Theta\}\,\phi_n'(\vec{r}';R); \qquad \text{(II-60c)}$$

where $\hat{L}_{x'}$, $\hat{L}_{y'}$, $\hat{L}_{z'}$ are the components of the electronic orbital angular momentum in the rotating frame. The components of the vector, $\underline{\vec{P}}(R)$, are then given by[7a,32]

$$\vec{P}_{jn}(R) = P^R_{jn}\,\hat{z}' + P^\Theta_{jn}\,\hat{x}' + P^\Phi_{jn}\,\hat{y}', \qquad \text{(II-61)}$$

where $\hat{x}'$, $\hat{y}'$, $\hat{z}'$ are the unit axis vectors in the rotating frame, and

$$P^R_{jn} = -i\hbar\,\langle\phi_j|(\partial/\partial R)_{\vec{r}'}|\phi_n\rangle, \qquad \text{(II-62a)}$$

$$P^\Theta_{jn} = -R^{-1}\,\langle\phi_j|\hat{L}_{y'}|\phi_n\rangle, \qquad \text{(II-62b)}$$

$$P^\Phi_{jn} = +R^{-1}\,\{\langle\phi_j|\hat{L}_{x'}|\phi_n\rangle - \cot\Theta\,\langle\phi_j|\hat{L}_{z'}|\phi_n\rangle\}. \qquad \text{(II-62c)}$$

For convenience, I have dropped the primes on $\phi_n'(\vec{r};R)$. The components of $\underline{\vec{A}}(R)$ are simply defined by the components of the vector, $\vec{s}$, in the rotating frame.

In the classical trajectory description, the motion of the nuclei is confined to a plane, and, without loss of generality, we can take this as the (x',z') plane. Moreover, to compute the matrix elements, P^Θ_{jn} and P^Φ_{jn}, we require in both cases, only the matrix elements of the ladder operators, $\hat{L}_\pm'$. Therefore, the behaviour of the angular couplings will be fully covered by a study of a single angular component, which we [illegible] to be $(P^\theta_{jn}+A^{x'}_{jn})$. This coupling is just the quantum mechanical Coriolis coupling, seen by an electron in the rotating frame.

Asymptotically, the components of $\underline{\vec{P}}(R)+\underline{\vec{A}}(R)$ are just [cf. equation (II-55)]

$$P^R_{jn} + A^{z'}_{jn} = -i\hbar \langle \phi_{j_J} | (\partial/\partial R)_{\vec{r}_J} | \phi_{n_J} \rangle, \qquad \text{(II-63a)}$$

and

$$P^\theta_{jn} + A^{x'}_{jn} = - R^{-1} \langle \phi_{j_J} | \hat{L}^J_{y'} | \phi_{n_J} \rangle. \qquad \text{(II-63b)}$$

CHAPTER III

BORN-OPPENHEIMER WAVEFUNCTIONS

A. Introduction

In this chapter, I shall describe the computation of the eigenfunctions for two-centre, fixed-nuclei, one-electron systems--the Born-Oppenheimer wavefunctions. These states are solutions of the adiabatic Schrödinger equation,

$$\{(\hbar^2/2m_0)\ \nabla_r^2 + e^2(Z_A/r_A+Z_B/r_B) + \varepsilon\}\ \Psi(\vec{r};R) = 0, \quad \text{(III-1)}$$

where $\varepsilon = \varepsilon'(R) - Z_A Z_B e^2/R$ is the electronic energy. ε may be either positive (the electronic continuum) or negative (discrete bound states).

It is well known[35] that the Schrödinger equation (1) is separable in prolate spheroidal co-ordinates, (ξ,η,ϕ), where (see figure 3)

$$\xi = (r_A+r_B)/R, \qquad \eta = (r_A-r_B)/R, \qquad \phi = \text{azimuthal angle} \quad \text{(III-2)}$$

$$1 \le \xi < \infty \qquad -1 \le \eta \le +1 \qquad 0 \le \phi \le 2\pi;$$

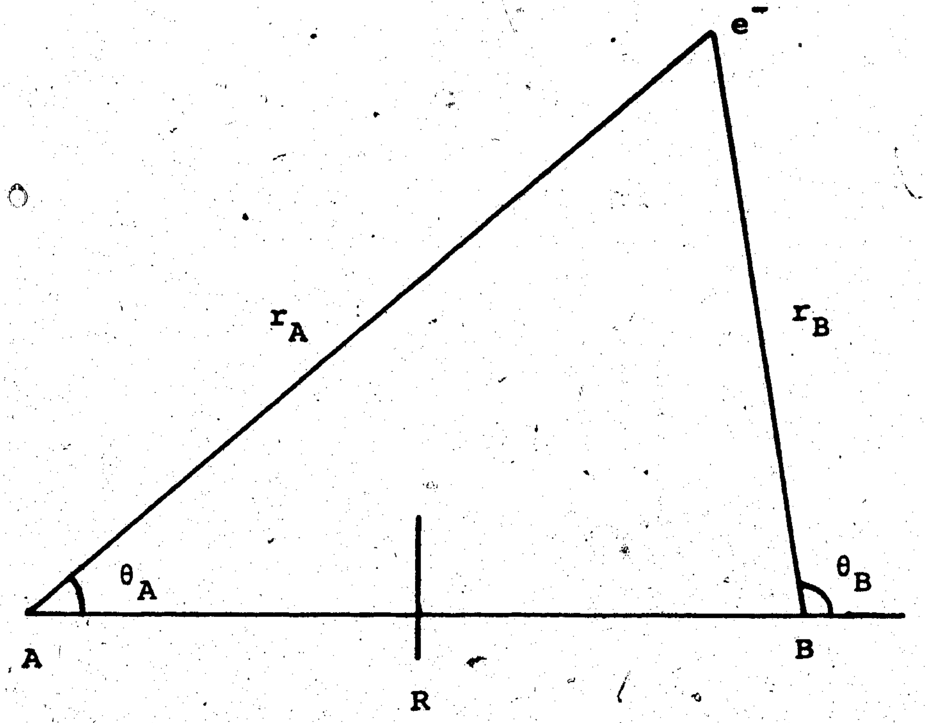

Figure 3. Spheroidal Co-ordinates

$\xi = (r_A+r_B)/R, \quad \eta = (r_A-r_B)/R, \quad \phi$

and r_A and r_B are the distances of the electron from the nuclei A and B, respectively. The electron has mass, m_0, and we use the Bohr radius, a_0, as the unit of length; the energy is in Rydbergs (1 Ry. = $e^2/2a_0$ = 0.5 au). Ψ can be written

$$\Psi(\vec{r};R) = X(\xi)\,S(\eta)\,\Phi(\phi), \tag{III-3}$$

and the separated equations for the factors are

$$d^2\Phi/d\phi^2 + m^2\,\Phi = 0, \tag{III-4}$$

$$d/d\eta\ \{(1-\eta^2)dS/d\eta\} + \{p\eta \pm c^2\eta^2 + A - m^2/(1-\eta^2)\}S = 0, \tag{III-5}$$

$$d/d\xi\ \{(\xi^2-1)dX/d\xi\} + \{q\xi \mp c^2\xi^2 - A - m^2/(\xi^2-1)\}X = 0; \tag{III-6}$$

where the parameters, p, q, and c^2, are defined

$$p = R(Z_B - Z_A), \qquad q = R(Z_B + Z_A), \tag{III-7a}$$

$$c^2 = \mp \tfrac{1}{4}\,\varepsilon\,R^2. \tag{III-7b}$$

A and m^2 are the separation constants; m is the modulus of the azimuthal quantum number. In equations (III-5) to (III-7), where a "±" appears, the upper sign gives the bound state equations, while the lower gives those corresponding to the continuum.

In the united atom limit, equation (III-5) tends to the equation for the associated Legendre function, $P_L^m(\eta)$, with $A = L(L+1)$; and equation (III-6) becomes the radial equation for either the spherical Coulomb function, or the associated Laguerre function.[36] The wavefunction for the azimuthal co-ordinate is, of course, just

$$\Phi(\phi) = (2\pi)^{-\frac{1}{2}} \exp(\pm im\phi), \text{ with } m = 0, 1\ldots \quad \text{(III-8)}$$

In sections B and C, I will discuss the solutions of equations (III-5) and (III-6), for bound and continuum electronic states, respectively.

B. Bound States

1. Background

The solution of equation (III-1) has received considerable attention for negative energies. Subject to the usual conditions that the wavefunction be square-integrable, continuous, and have continuous first derivatives, the coupled equations, (III-5) and (III-6), have simultaneous solutions only for discrete pairs of values of the parameters, A and c. In the limits, $R\to 0$ and $R\to\infty$, simple closed formulae exist for the energies and wavefunctions, but, in general, we must solve the equations numerically.

Various authors have complied extensive tables of the eigenparameters, both for H_2^+,[37-40] and for unequal nuclear charges.[41,42] The formal properties of the solutions have been examined in great detail by Power.[43] To compute solutions, I used a method based on that given by Bates and Carson[41] for HeH^{++}.

For a given bound state, the calculation of the eigenvalues of A and c proceeds as follows. At each consecutive R-value,

i. Guess approximate values for the eigenvalue, c_g, and separation constant, A_g

ii. Guess a spread, δ, such that the true eigenvalue is expected to lie between $c_g-\delta$ and $c_g+\delta$

iii. For a series of values of c, between $c_g-\delta$ and $c_g+\delta$, compute the value of A which gives the regular solution to equation (III-5), the angular equation

iv. Use this set of pairs of values of A and c to determine A as a suitable polynomial function of c

v. Using this A(c), compute the value of c which gives the regular solution to equation (III-6), the radial equation. This is the desired eigenvalue, c

vi. Now go back to the angular equation, and compute the separation constant corresponding to this value of c

Once A and c have been found, the corresponding eigenfunctions can be computed fairly easily.

In the next two sections, I shall describe the computation of solutions to the angular and radial equations in more detail.

2. Angular Equation

$$d/d\eta \; \{(1-\eta^2)dS/d\eta\} + \{p\eta+c^2\eta^2+A-m^2/(1-\eta^2)\} \; S = 0. \quad \text{(III-9)}$$

We require solutions to (III-9) which are regular in the interval, $-1 \leq \eta \leq +1$. Following Bates and Carson,[41] we write

$$S(\eta) = \exp(-c\eta) \sum_{L=m} d_L \, P_L^m(\eta), \qquad \text{(III-10)}$$

where $P_L^m(\eta)$ is the L'th associated Legendre function. Substituting (III-10) into (III-9), and using the recursion relations satisfied by the P_L^m's, we obtain, after some manipulation,

$$\Sigma \, d_L \, \{P_{L-1}^m \, (p-2cL)(L+m)/(2L+1) + P_L^m \, [c^2+A-L(L+1)]$$

$$+ P_{L+1}^m \, [p+2c(L+1)](L-m+1)/(2L+1)\} = 0. \qquad \text{(III-11)}$$

Since the P_L^m's form a complete, orthogonal set, equation (III-11) can only be satisfied if the coefficient of P_L^m vanishes identically, for each L. This leads to a three-term recursion formula linking the d_L's:

$$d_{L-1}\,(p+2cL)(L-m)/(2L-1) + d_L\,[c^2+A-L(L+1)]$$

$$+ d_{L+1}\,[p-2c(L+1)](L+m+1)/(2L+3) = 0. \qquad \text{(III-12)}$$

For very large L, the coefficients satisfy either

$$d_{L+1} \approx -\,(L/c)\,d_L \qquad \text{(III-13a)}$$

or

$$d_L \approx +\,(c/L)\,d_{L-1}. \qquad \text{(III-13b)}$$

Clearly, we require solutions which behave like (III-13b); for a given c, these only exist for particular values of A --the eigenvalues. To determine these, I used Ince's well known method for finding the eigenvalues of a tridiagonal matrix,[44] as described by Stratton et al.[45]

For computing the function, $S(\eta)$, it is not convenient to use the expansion given in (III-10); convergence of the series is often poor, even at moderate internuclear separations, and the evaluation of integrals over η is awkward. I therefore chose to use the approach introduced by Helfrich[46] and expressed the wavefunction as

$$S(\eta) = \sum_{L=m} \tilde{d}_L\, P_L^{\,m}(\eta). \qquad \text{(III-14)}$$

This gives a five-term recursion formula for the $\tilde{d}_L$'s:

$$\tilde{d}_{L-2}\, c^2(L-m)(L-m-1)/[(2L-3)(2L-1)] + \tilde{d}_{L-1}\, p(L-m)/(2L-1)$$
$$+ \tilde{d}_L\, \{c^2[2L(L+1)-2m^2-1]/[(2L+3)(2L-1)] - L(L+1) + A\}$$
$$+ \tilde{d}_{L+1}\, p(L+m+1)/(2L+3) + \tilde{d}_{L+2}\, c^2(L+m+2)(L+m+1)/[(2L+5)$$
$$(2L+3)] = 0. \qquad \text{(III-15)}$$

The technique for finding the coefficients, $\tilde{d}_L$, given the eigenvalue, A, is described by Wilkinson[47] and the series (III-14) is truncated when the $\tilde{d}_L$'s become sufficiently small. Of course, the wavefunction cannot be computed until the eigenvalue, c, has been found.

Let us now turn, then, to the solution of the radial equation. We will assume that, in the vicinity of the desired eigenvalue, A is known as a function of c; in my programme, I chose to fit the computed separation constants to a cubic polynomial in c, by the least squares method.

3. Radial Equation

$$d/d\xi\ \{(\xi^2-1)\,dX/d\xi\} + \{q\xi - c^2\xi^2 - A - m^2/(\xi^2-1)\}\ X = 0. \qquad \text{(III-16)}$$

At large ξ, the two linearly-independent solutions to equation (III-16) behave like $\exp(\pm c\xi)$. Clearly, we are interested in the exponentially damped solution, and, once again following Bates and Carson,[41] we use the transformation due to Jaffé:

$$X(\xi) = (\xi+1)^{q/2c-1} \{(\xi-1)/(\xi+1)\}^{m/2} \exp(-c\xi)$$

$$\sum_{n=0} a_n \{(\xi-1)/(\xi+1)\}^n \quad \text{(III-17)}$$

If we substitute (III-17) into (III-16), collect terms in powers of $(\xi-1)/(\xi+1)$, we obtain, after a lot of algebra, a three term recursion formula linking the a_n's,

$$a_{n-1}\,(n+m-q/2c)(n-q/2c) + a_n\,\{(2n+m+1)(q/2c-2c-1)-2n(n+m)$$
$$+q-A-c^2\} + a_{n+1}\,(n+1)(n+m+1) = 0, \qquad \text{(III-18)}$$

with $a_{-1} = 0$, and $a_0 = 1$.

Given $A(c)$, Ince's method[44] yields the desired eigenvalue, c, and the coefficients, a_n, in equation (III-17). The eigenenergy is then given simply by

$$\varepsilon = -\,(2c/R)^2. \qquad \text{(III-19)}$$

4. Normalisation

The wavefunction is normalised in the usual way, i.e., we set

$$\langle\Psi|\Psi\rangle = 1. \qquad \text{(III-20)}$$

The volume element in spheroidal co-ordinates is

$$d\tau = (R/2)^3\,(\xi^2-\eta^2)\,d\xi d\eta d\phi, \qquad \text{(III-21)}$$

and hence, we have to evaluate

$$N^2 = (R/2)^3\,\{\int_{-1}^{+1}S^2(\eta)\,d\eta\,\int_1^\infty X^2(\xi)\,\xi^2 d\xi\ -$$

$$\int_{-1}^{+1}S^2(\eta)\,\eta^2 d\eta\,\int_1^\infty X^2(\xi)\,d\xi\}. \qquad \text{(III-22)}$$

I chose to normalise the coefficients, $\tilde{d}_L$, such that

$$\int_{-1}^{+1}S^2(\eta)\,d\eta = 1. \qquad \text{(III-23)}$$

The η-integrals can be evaluated analytically, using the orthogonality relation satisfied by the Legendre functions,

$$\int_{-1}^{+1} P_j^{\,m}(\eta)P_n^{\,m}(\eta)\,d\eta = 2/(2j+1)\ \ (j+m)!/(j-m)!\ \delta_{jn}; \qquad \text{(III-24)}$$

and we find that

$$\gamma^2 = \int_{-1}^{+1}S^2(\eta)\,\eta^2 d\eta = \sum_{L=m} 2(L+m)!/(L-m)!\ \{\tilde{d}_L^{\,2}\ [2L-1+2(L^2-m^2)]$$

$$+\ 2\,\tilde{d}_{L+1}\tilde{d}_{L-1}\ [L(L+1)-m(m+1)]\}/[(2L-1)(2L+1)(2L+3)]. \qquad \text{(III-25)}$$

Thus, equation (III-22) reduces to

$$N^2 = (R/2)^3 \int_1^\infty X^2(\xi)\ (\xi^2-\gamma^2)\ d\xi. \qquad \text{(III-26)}$$

This integral has to be done numerically, and I chose to evaluate it by Gaussian quadrature. Since integrals of this general form appear several times, I will describe the method used for evaluating them in some detail.[48] They can all be written

$$I(\alpha) = (R/2)^3 \int_1^\infty \exp(-\alpha\xi)\ g(\xi)\ d\xi. \qquad \text{(III-27)}$$

For example, in equation (III-26), $\alpha = 2c$. If we change the variable to $x = \alpha(\xi-1)$, we find that

$$I(\alpha) = (R/2)^3 e^{-\alpha}/\alpha \int_0^\infty e^{-x}\ g(1+x/\alpha)\ dx; \qquad \text{(III-28a)}$$

this can be evaluated by Gauss-Laguerre quadrature, giving

$$I(\alpha) \simeq (R/2)^3 e^{-\alpha}/\alpha \sum_{i=1}^{N} w_i\ g(\xi_i), \qquad \text{(III-28b)}$$

where

$$\xi_i = 1 + x_i/\alpha. \qquad \text{(III-28c)}$$

The integration points, x_i, and weights, w_i, are given in

Abramowitz and Stegun[49] for various values of N, and I used a 28-point truncation of the 64-point formula, although this was probably over-cautious. Exploratory calculations showed that this formula will produce about 12 (1) figure accuracy for a wide variety of functions, g(x), whereas the error in the wavefunctions is about one part in 10^6.

The programme computes the value of N, and stores it for later use. Let us now turn to the problem of computing the continuum wavefunctions.

C. Continuum States[50]

1. Background

The electronic continuum states for the two-centre, one-electron system have received very little attention, compared with that given to the bound-state functions. Bates, Opik and Poots[51] describe the solution for H_2^+, in connection with photo-ionisation cross sections for the molecule-ion. Recently, Ponomarev and Somov[52] have described the solution for HeH^{++}, and an incorrect solution (later corrected) for arbitrary charges has been published by Greenland.[53] I have used a method similar to that of Ponomarev and Somov.[52] Regular solutions exist for all positive energies, and for discrete values of the separation constant, A.

2. Angular Equation

$$d/d\eta \{(1-\eta^2)dS/d\eta\} + \{p\eta-c^2\eta^2+A-m^2/(1-\eta^2)\} S = 0. \quad \text{(III-29)}$$

We require solutions to equation (III-29) which are regular in the interval, $-1 \leq \eta \leq +1$. Now, (III-29) is obtained from the corresponding bound state equation if we replace c by ic. This suggests that we can solve (III-29) in a manner analogous to that used for (III-9); we write

$$S(\eta) = \exp(-ic\eta) \sum_{L=m} d_L P_L^m(\eta), \qquad \text{(III-30)}$$

and we obtain a three-term recursion formula for the d_L's:

$$d_{L-1} (p+2icL)(L-m)/(2L-1) + d_L \{A-c^2-L(L+1)\} +$$

$$d_{L+1} \{p-2ic(L+1)\}(L+m+1)/(2L+3) = 0, \qquad \text{(III-31)}$$

with $d_{m-1} = 0$. The eigenvalues of A are real (as Ponomarev and Somov[52] point out, they depend only on the absolute values of the complex coefficients in (III-31)), and they can be determined by Ince's method[44] for a given continuum energy and R-value.

As with the bound state equation, the expansion, (III-30), does not provide a convenient representation of the wavefunction, and we express the solution as

$$S(\eta) = \sum_{L=m} \tilde{d}_L P_L^{\,m}(\eta), \qquad \text{(III-32)}$$

which yields a five-term recursion formula for the $\tilde{d}_L$'s:

$$\tilde{d}_{L-2}\, c^2 (L-m)(L-m-1)/[(2L-3)(2L-1)] - \tilde{d}_{L-1}\, p(L-m)/(2L-1) +$$

$$\tilde{d}_L \,\{L(L+1)-A+c^2[2L(L+1)-2m^2-1]/[(2L-1)(2L+3)]\} -$$

$$\tilde{d}_{L+1}\, p(L+m+1)/(2L+3) + \tilde{d}_{L+2}\, c^2 (L+m+2)(L+m+1)/[(2L+3)(2L+5)]$$

$$= 0. \qquad \text{(III-33)}$$

Given an eigenvalue, A, the $\tilde{d}_L$'s can again be computed by the method described in Wilkinson.[47] Notice that equations (III-29) to (III-33) can all be obtained from the corresponding bound state equations, (III-9,10,12,14,15), by replacing c with ic.

3. Radial Equation

$$d/d\xi\, \{(\xi^2-1)dX/d\xi\} + \{q\xi+c^2\xi^2-A-m^2/(\xi^2-1)\}\, X = 0. \qquad \text{(III-34)}$$

We require the solution of (III-34) which is regular at $\xi = 1$. At large ξ, this solution has the form

$$X^{reg}(\xi) \sim (B/r)\sin\{kr+\gamma\ln(kr)+\delta\}, \qquad \text{(III-35a)}$$

where

$$\gamma = q/(2c) = (Z_A+Z_B)/k, \qquad \text{(III-35b)}$$

$$c\xi \sim kr, \qquad k^2 = \varepsilon. \qquad \text{(III-35c)}$$

B is the normalisation constant, and δ is the phase shift.

Equation (III-34) is solved by starting the solution near the origin with a series expansion, and continuing this solution outward by numerical integration, until it can be matched with asymptotic solutions to determine the phase shift. The solution regular at $\xi = 1$ has the form

$$X(\xi) = \{(\xi-1)/(\xi+1)\}^{m/2} F(\xi), \qquad \text{(III-36)}$$

where $F(\xi)$ satisfies the equation

$$(\xi^2-1)F''(\xi) + 2(m+\xi)F'(\xi) + (c^2\xi^2+q\xi-A)F(\xi) = 0. \qquad \text{(III-37)}$$

Near the origin, this can be written as a power series in $(\xi-1)$,

$$F^{reg}(\xi) = \sum_{n=0} a_n (\xi-1)^n, \qquad \text{(III-38)}$$

and this yields a four-term recursion relation for the coefficients, a_n:

$$a_{n-2}\,c^2 + a_{n-1}\,(2c^2+q) + a_n\,[n(n+1)+c^2+q-A] +$$

$$2a_{n+1}\,(n+1)(n+m+1) = 0, \qquad \text{(III-39)}$$

where $a_{-2} = a_{-1} = 0$; and $a_0 = 1$.

The solution, $F^{reg}(\xi)$, is continued numerically by integration of (III-37) using a variable-step, Adams-Moulton-Bashforth, predictor-corrector method,[54] until a value of ξ suitable for matching $F^{reg}(\xi)$ with asymptotic solutions is reached. However, for evaluating integrals numerically, we have seen that the value of the integrand is required at s[illegible]ic values, ξ_i, whereas the A-M-B algorithm gives the function at successive points, separated by a predetermined step-size. The programme must thus include a modification to evaluate $F^{reg}(\xi_i)$: whenever the A-M-B integration passes one of the ξ_i, the programme pauses to use the fourth-order Runge-Kutta method[54] to calculate and store the $F^{reg}(\xi_i)$.

At large ξ, asymptotic solutions to (III-37) are

$$F^{\pm}(\xi) = (\xi+1)^{-1}\,\exp \pm i\{c\xi+\gamma \ln(\xi+1)\}\; u^{\pm}(\xi), \qquad \text{(III-40)}$$

and if we write

$$u^{\pm}(\xi) = \sum_{n=0} b_n^{\pm}\,\{2/[c(\xi+1)]\}^n, \qquad \text{(III-41)}$$

the coefficients satisfy a three-term recursion formula:

$$b^{\pm}_{n-1}\, c\{n(n+m)-\gamma^2 \mp i\gamma(2n+m)\} - b^{\pm}_{n}\, \{n(n+1)-\gamma^2+q+c^2-A$$

$$\mp i\gamma[(2n+1)-2c(2n+m+1)]\} \pm 4i\, b^{\pm}_{n+1}(n+1) = 0, \qquad \text{(III-42)}$$

with $b^{\pm}_{-1} = 0$, $b^{\pm}_{0} = 1$. Evidently, $u^{-}(\xi) = \{u^{+}(\xi)\}^{*}$. The expression, (III-41), is an asymptotic expansion; if ξ is large enough, it yields sufficiently accurate solutions, $F^{\pm}(\xi)$. The phase shift is determined by matching $F^{reg}(\xi)$ and $dF^{reg}(\xi)/d\xi$ to some suitable linear combination of the asymptotic solutions; that is, we write

$$F^{reg}(\xi) = D\,\{e^{i\alpha}\, F^{+}(\xi) + e^{-i\alpha}\, F^{-}(\xi)\}$$

$$\text{(III-43a)}$$

$$[F^{reg}(\xi)]' = D\,\{e^{i\alpha}\, [F^{+}(\xi)]' + e^{-i\alpha}\, [F^{-}(\xi)]'\}$$

and determine α. We find that

$$\tan\alpha = \mathrm{Re}(h^{\pm})/\mathrm{Im}(h^{\pm}) \qquad \text{(III-43b)}$$

$$h^{\pm} = \{u^{\pm}(\xi)' - u^{\pm}(\xi)[w(\xi) \mp ig(\xi)']\}\, \exp{\pm ig(\xi)}, \qquad \text{(III-43c)}$$

where

$$w(\xi) = [F^{reg}(\xi)]'/F^{reg}(\xi) + (\xi+1)^{-1} \qquad \text{(III-44a)}$$

and

$$g(\xi) = c\xi + \gamma\ln(\xi+1). \qquad \text{(III-44b)}$$

From equations (III-40) and (III-43), it follows that

$$\chi^{reg}(\xi) \sim \{C/(\xi+1)\}\,\sin\{c\xi+\gamma\ln[c(\xi+1)\text{[illegible]}\}, \qquad \text{(III-45a)}$$

$$\delta = \alpha - \gamma\ln(c) + \pi/2, \qquad \gamma = c\text{[illegible]} \qquad \text{(III-45b)}$$

In the united atom l[illegible] tends to the appropriate Coulomb scattering p[illegible]

$$\lim_{R\to 0} \delta = \sigma_L - (L\pi/2) + \gamma\ln(2), \qquad \text{(III-46a)}$$

$$\sigma_L = \mathrm{Arg}\{\Gamma(L+1-i\gamma)\}. \qquad \text{(III-46b)}$$

Levy and Thorson[1b] have reported phase shifts for the H_2^+ problem, but these contain an arithmetic error. The correct phases are obtained by subtracting $c = \frac{1}{2}kR$ from their values; other quantities, such as the matrix elements they reported, are unaffected. This error has also been noted by Greenland and Greiner.[53b]

4. Normalisation

The wavefunction is normalised so that the density of continuum levels is included,

$$\langle \Psi_{\varepsilon' L' m'} | \Psi_{\varepsilon L m} \rangle = \delta(\varepsilon' - \varepsilon)\, \delta_{L'L}\, \delta_{m'm}. \qquad \text{(III-47)}$$

If the coefficients in the angular eigenfunction are normalised such that

$$\int_{-1}^{+1} S^2(\eta)\, d\eta = 1, \qquad \text{(III-48)}$$

this requires[51,52]

$$C = 2/(2\pi c R)^{1/2} = 2/[R(\pi k)^{1/2}] \qquad \text{(III-49)}$$

If one wishes to express the energy in atomic units (2 Ry. = 1 au), one has to be rather careful at this point. The density of states, $dn/d\varepsilon$, in atomic units is twice that in Rydbergs; and hence, $C_{au} = 2^{1/2} C_{Ry}$. The programme computes C (in Rydbergs) and stores it for later use.

5. Remarks

The representation of the solutions differs in some ways from that given by Ponomarev and Somov.[52]

a. I use an expansion in Legendre polynomials to compute the angular solution, whereas they employ a power series near $\xi = -1$, followed by numerical integration.

b. Using the extended asymptotic solutions for the radial wavefunction (equations (III-40) to (III-42)) allows more rapid calculation of both phase shifts and wavefunctions. The point, ξ^*, at which the numerical solution is matched to the asymptotic solution, is given by

$$c\xi^* \simeq 3\gamma; \qquad \text{(III-50a)}$$

Ponomarev and Somov[52], state that they found

$$c\xi^* \simeq 50\,|A-c^2+\gamma^2|. \qquad \text{(III-50b)}$$

c. The representation of $X^{reg}(\xi)$ near $\xi = 1$ is also slightly different, but this is not significant.

P. T. Greenland[53] proposes a solution for the continuum states which is not correct. In particular:

a. He imposes constraints which imply that the states, $S(\eta)$, are parity eigenstates, regardless of the charge asymmetry; this is clearly false

b. He attempts to compute $X^{reg}(\xi)$ by fixing the asymptotic behaviour of the solution, rather than the behaviour at $\xi = 1$.

Let us now look at some representative results.

6. Results

The notation we use labels the continuum states with the energy, ε, the united-atom-limit, angular momentum quantum number, L, and m, the modulus of the azimuthal quantum number.

Table 1 gives some representative values for the separation constants and phase shifts in HeH^{++}; data shown are for $\varepsilon = 1.0$ Ry., and the states, sσ (L=m=0), pσ (L=1, m=0), and pπ (L=m=1), for internuclear separations, $0 \leq R \leq 12$ au. In the united atom limit, the phase shifts all agree with the appropriate Coulomb phases ((III-45) and (III-46)) modulo 2π. Tables 2 to 4 illustrate the behaviour of the expansion coefficients, $\tilde{d}_L$, of the angular eigenfunctions for the same states, for $0 \leq R \leq 6$ au.

Figure 4 shows the separation constants for the model system with $(Z_A/Z_B) = 1.2$, at energy $\varepsilon = 0.5$ Ry., for the states, sσ, pσ, pπ, dσ, dπ, dδ. The results may be applied directly to a real bare-nucleus system with Z_A', Z_B' integers (e.g., 12, 10), by scaling all distances as $(Z_B')^{-1}$, all energies as $(Z_B')^2$.

Figures 5 and 6 depict phase shifts for the model system at $\varepsilon = 0.5$ Ry., and for HeH^{++} at $\varepsilon = 1.0$ Ry., for the states, pπ, dσ, dπ, fσ, dδ, fπ, gσ, fδ, gπ, hσ. It is interesting to note the systematic interleaving and ordering of the phases in the large R region. They appear to be grouped according to the value of (L+m), with phase shifts decreasing as that index increases; within any group of given (L+m), they are ordered by the value of L, with phase shifts decreasing as L increases. Members of a group never cross each other. This behaviour seems to be quite general for all charge ratios and energies.

TABLE 1

SEPARATION CONSTANTS AND PHASE SHIFTS FOR HeH^{++}; ε = 1.0 Ry. and δ IS IN UNITS OF π

	sσ WAVE		pσ WAVE		pπ WAVE	
R	A	δ	A	δ	A	δ
0.0	0.000000	0.32661	2.000000	1.42903	2.000000	1.42903
0.5	-0.019726	0.21542	2.061212	1.48671	2.000083	1.39992
1.0	-0.067583	0.08905	2.231426	1.54631	2.001287	1.33885
1.5	-0.119657	-0.02076	2.480920	1.52845	2.006210	1.26945
2.0	-0.154305	-0.11892	2.780038	1.47423	2.018430	1.19966
2.5	-0.157431	-0.20910	3.106771	1.40952	2.041735	1.13187
3.0	-0.121627	-0.29334	3.448244	1.34357	2.079508	1.06667
3.5	-0.044246	-0.37280	3.800033	1.27934	2.134352	1.00411
4.0	0.074055	-0.44815	4.164259	1.21740	2.207954	0.94408
4.5	0.230295	-0.51974	4.547059	1.15752	2.301088	0.88642
5.0	0.419874	-0.58781	4.956207	1.09926	2.413727	0.83100
5.5	0.637180	-0.65248	5.399372	1.04218	2.545180	0.77770
6.0	0.876168	-0.71384	5.882991	0.98597	2.694259	0.72643
6.5	1.130917	-0.77200	6.411565	0.93045	2.859430	0.67709
7.0	1.396101	-0.82707	6.987263	0.87558	3.038956	0.62962
7.5	1.667318	-0.87921	7.609767	0.82142	3.231025	0.58394
8.0	1.941226	-0.92858	8.276389	0.76813	3.433846	0.53999
8.5	2.215513	-0.97539	8.982417	0.71591	3.645729	0.49768
9.0	2.488734	-1.01984	9.721666	0.66497	3.865132	0.45694
9.5	2.760112	-1.06213	10.487144	0.61552	4.090694	0.41771
10.0	3.029326	-1.10245	11.271748	0.56773	4.321242	0.37990
10.5	3.296346	-1.14098	12.068871	0.52174	4.555787	0.34345
11.0	3.561303	-1.17788	12.872869	0.47758	4.793513	0.30828
11.5	3.824407	-1.21327	13.679304	0.43529	5.033756	0.27432
12.0	4.085888	-1.24730	14.484988	0.39480	5.275984	0.24149

TABLE 2

THE COEFFICIENTS OF THE η-EXPANSION (EQUATION (III-32) OF TEXT), FOR HeH^{++}, sσ WAVE, AND ε = 1.0 Ry.

R	$\tilde{d}_0$	$\tilde{d}_1$	$\tilde{d}_2$	$\tilde{d}_3$	$\tilde{d}_4$	$\tilde{d}_5$	$\tilde{d}_6$	$\tilde{d}_7$	$\tilde{d}_8$	$\tilde{d}_9$	$\tilde{d}_{10}$
0.0	.707107										
0.5	.700208	-.170628	.004568	.000240	-.000008						
1.0	.683878	-.311121	.014949	.001820	-.000115	-.000003					
1.5	.665665	-.412656	.024853	.005706	-.000474	-.000021	.000002				
2.0	.650039	-.481407	.029656	.012478	-.001179	-.000087	.000011				
2.5	.638317	-.526306	.027074	.022450	-.002210	-.000262	.000033	.000001			
3.0	.630353	-.554306	.016244	.035753	-.003433	-.000638	.000078	.000005	-.000001		
3.5	.625537	-.570019	-.003000	.052358	-.004609	-.001336	.000156	.000016	-.000002		
4.0	.623164	-.576374	-.030445	.072074	-.005405	-.002506	.000272	.000041	-.000005		
4.5	.622536	-.575259	-.065591	.094533	-.005412	-.0043[illegible]	.000422	.000093	-.000011	-.000001	
5.0	.622989	-.567975	-.107631	.119181	-.004173	-.00[illegible]	.000589	.000190	-.000021	-.000003	
5.5	.623910	-.555550	-.155427	.145288	-.001234	-.01[illegible]	.000739	.000358	-.000035	-.000007	.000001
6.0	.624759	-.538926	-.207526	.171999	.003810	-.015079	.000817	.000627	-.000054	-.000015	.000002

TABLE 3

THE COEFFICIENTS OF THE η-EXPANSION (EQUATION (III-32) OF TEXT),

FOR HeH^{++}, pσ WAVE, AND ε = 1.0 Ry.

$\tilde{R}$	$\tilde{d}_0$	$\tilde{d}_1$	$\tilde{d}_2$	$\tilde{d}_3$	$\tilde{d}_4$	$\tilde{d}_5$	$\tilde{d}_6$	$\tilde{d}_7$	$\tilde{d}_8$	$\tilde{d}_9$	$\tilde{d}_{10}$
0.0		1.224745									
0.5	.098436	1.210212	-.102610	.000050	.000122	-.000001					
1.0	.178918	1.173840	-.208420	.000731	.000976	-.000022	-.000002				
1.5	.235470	1.127999	-.319564	.003224	.003311	-.000120	-.000012				
2.0	.270587	1.080113	-.435224	.008560	.007888	-.000412	-.000049	.000003			
2.5	.288590	1.033305	-.551100	.016928	.015398	-.001070	-.000147	.000013	.000001		
3.0	.293273	.989604	-.660940	.027308	.026359	-.002274	-.000360	.000039	.000002		
3.5	.287774	.951176	-.759000	.037624	.041057	-.004154	-.000763	.000096	.000007	-.000001	
4.0	.274718	.919985	-.841766	.045320	.059585	-.005730	-.001454	.000204	.000018	-.000003	
4.5	.256240	.897166	-.908173	.047964	.081919	-.009891	-.002556	.000386	.000040	-.000007	
5.0	.234028	.882806	-.958812	.043602	.107966	-.013391	-.004221	.000660	.000083	-.000016	-.000001
5.5	.209442	.876106	-.995017	.030844	.137577	-.016869	-.006624	.001043	.000162	-.000030	-.000002
6.0	.183638	.875686	-1.018288	.008838	.170535	-.019860	-.009964	.001537	.000297	-.000055	-.000005

TABLE 4

THE COEFFICIENTS OF THE η-EXPANSION (EQUATION (III-32) OF TEXT), FOR HeH^{++}, pπ WAVE, AND ε = 1.0 Ry.

R	$\tilde{d}_1$	$\tilde{d}_2$	$\tilde{d}_3$	$\tilde{d}_4$	$\tilde{d}_5$	$\tilde{d}_6$	$\tilde{d}_7$	$\tilde{d}_8$	$\tilde{d}_9$
0.0	.866025								
0.5	.864693	-.035790	-.000005	.000021					
1.0	.860935	-.069887	-.000083	.000167	-.000002				
1.5	.855372	-.100935	-.000394	.000547	-.000011	-.000001			
2.0	.848796	-.128100	-.001155	.001245	-.000031	-.000006			
2.5	.841956	-.151061	-.002576	.002315	-.000062	-.000016	.000001		
3.0	.835430	-.169885	-.004832	.003785	-.000100	-.000039	.000002		
3.5	.829584	-.184867	-.008040	.005660	-.000135	-.000080	.000004	.000001	
4.0	.824600	-.196410	-.012262	.007923	-.000149	-.000147	.000007	.000002	
4.5	.820512	-.204940	-.017505	.010545	-.000120	-.000251	.000011	.000004	
5.0	.817257	-.210865	-.023732	.013481	-.000022	-.000399	.000016	.000007	
5.5	.814713	-.214558	-.030872	.016679	.000175	-.000602	.000021	.000013	-.000001
6.0	.812724	-.216353	-.038821	.020078	.000497	-.000869	.000024	.000022	-.000001

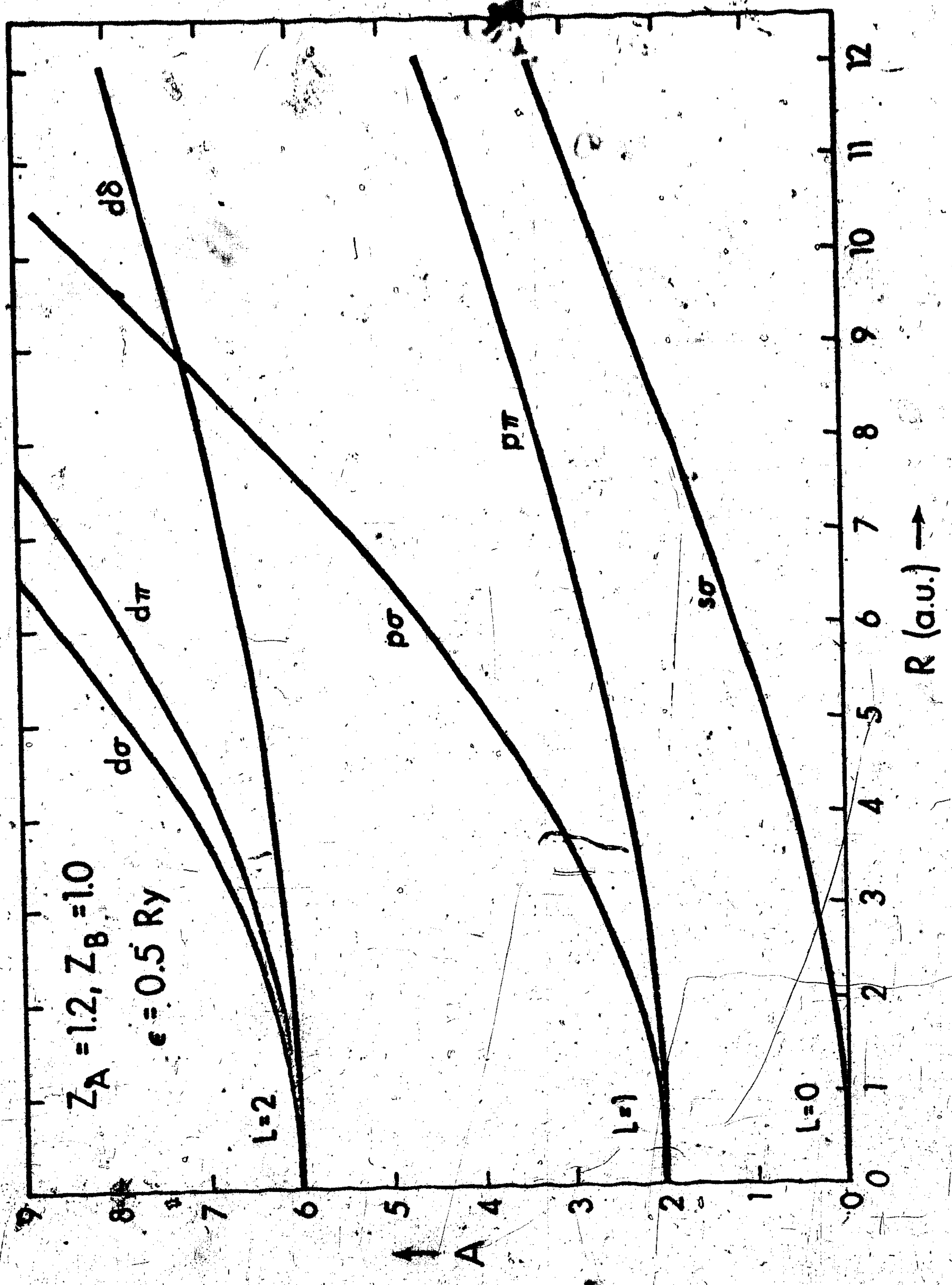

Figure 4. Continuum separation constants, for s, p, and d waves

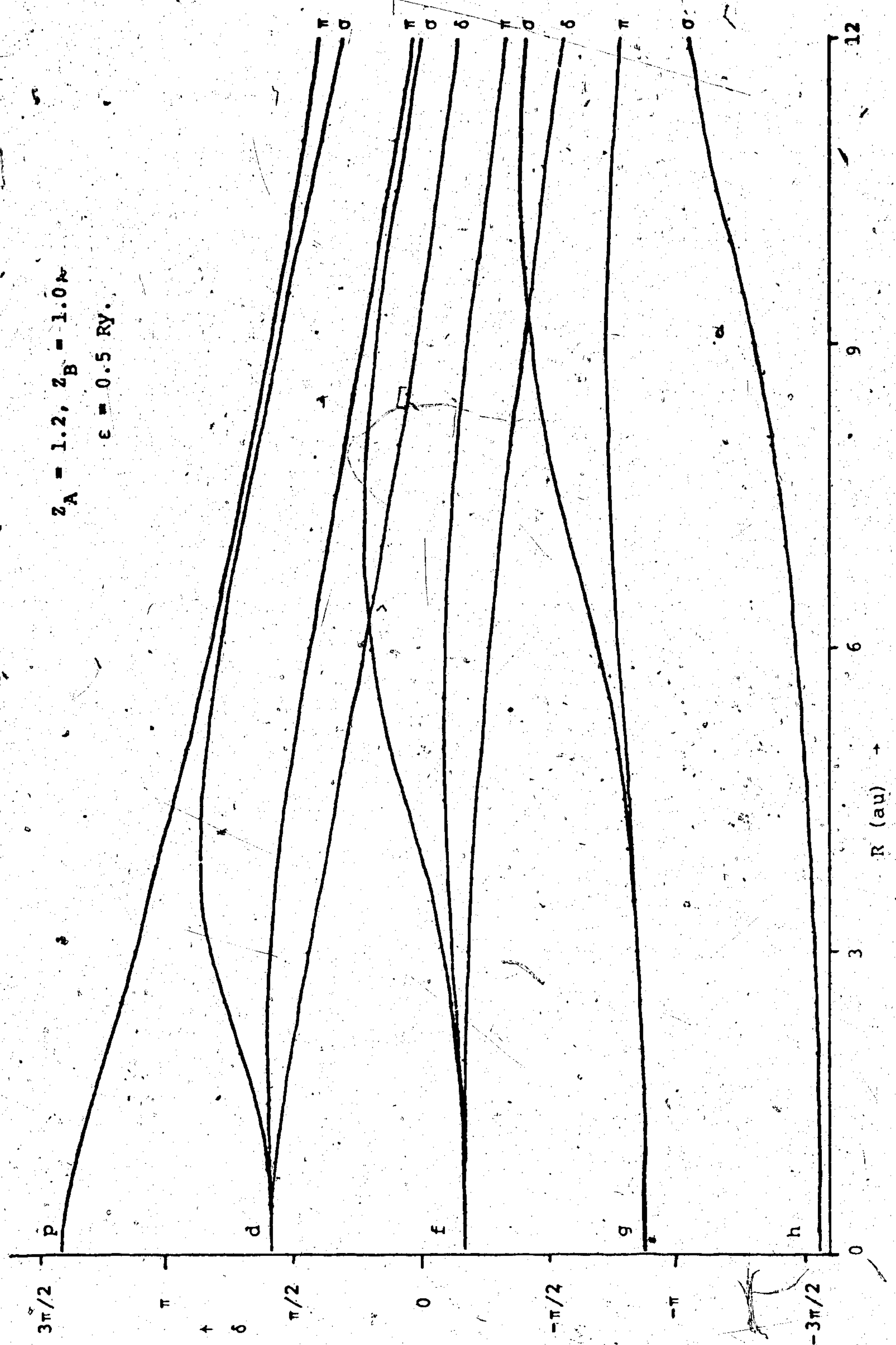

Figure 5. Phase shifts for model system

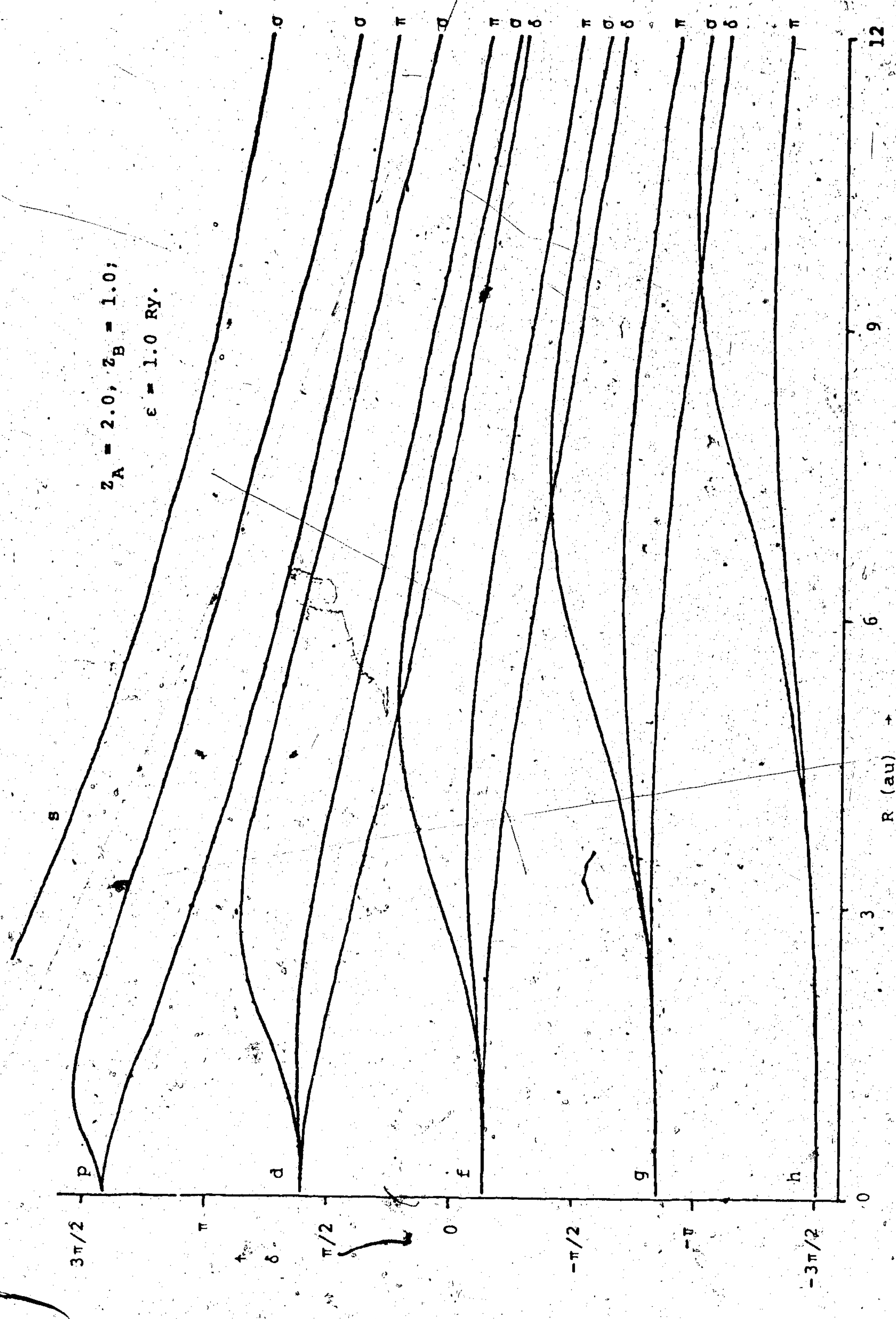

Figure 6. Phase shifts for HeH^{++}

CHAPTER IV

COMPUTATION OF MATRIX ELEMENTS

A. Introduction

In chapter II, we saw how to formulate the theory of slow atomic collisions in a way which takes account of electron translation. I showed that the nonadiabatic couplings which appear in pss theory must be modified by important corrections. These corrections exactly cancel the spurious asymptotic pss couplings, and also produce substantial reductions in the effective coupling matrix elements at finite internuclear separations. The derivation is approximate, since it assumes that the heavy particles behave classically, but the main conclusions are the same as those in the rigorous, quantum mechanical derivation, given by Thorson and Delos.[7]

The formulation employs a switching function $f(r;R)$, to represent the translational motion of the electron as a local function of its position. Apart from the asymptotic constraints (f tends to +1 on B, and -1 on A), f is undefined, and the derivation provides no criteria for its specification. The problem of choosing f remains unsolved. Many of the obvious defects of pss theory are removed by any reasonable choice of f which meets the asymptotic constraints, but there are many transitions for which the corrected matrix elements are very sensitive to that choice. Studies of the f-dependence can provide useful insight, particularly if the behaviour of the matrix elements follows some obvious pattern.

The corrected couplings for transitions from low-lying bound states to the electronic continuum are known[2] to be highly sensitive to variations in f. In this chapter, I will describe the computation of matrix elements for these transitions. The motivation for, and the results of, these calculations will be discussed in detail in the next chapter.

B. Coupling Matrix Elements

In pss theory, the matrix elements for nonadiabatic coupling are defined

$$\vec{P}_{jn}(R) = -i\hbar \langle \phi_j | (\vec{\nabla}_R)_{\vec{r}} | \phi_n \rangle , \qquad \text{(IV-1)}$$

where $\phi_n(\vec{r};\vec{R})$ are the Born-Oppenheimer, molecular electronic states; $\vec{R}$ is the internuclear co-ordinate, and $\vec{r}$ is the electron co-ordinate, measured from the <u>centre of mass of the nuclei</u> (CMN). $\vec{P}_{jn}$ has "angular" as well as "radial" components, since the molecular states are defined in a rotating frame, in which Coriolis forces appear.

In chapter II, I showed that, in the corrected theory, $\underline{\vec{P}}(R)$ is simply replaced by $\underline{\vec{P}}^g(R) + \underline{\vec{A}}^g(R)$, where

$$\vec{P}^g_{jn} = -i\hbar \langle\phi_j|(\vec{\nabla}_R)_{\vec{r}_g}|\phi_n\rangle, \tag{IV-2}$$

and

$$\vec{A}^g_{jn} = (im/\hbar) \langle\phi_j|[h_{BO},\vec{s}^g]|\phi_n\rangle, \tag{IV-3}$$

with

$$\vec{s}^g = \tfrac{1}{2} f(\vec{r};\vec{R})\, \vec{r}_g; \tag{IV-4}$$

h_{BO} is the Born-Oppenheimer electronic Hamiltonian, and $\vec{r}_g$ is the electron co-ordinate, measured from the geometric centre, rather than the CMN.

It is sufficient to compute the radial component and one angular component of the above couplings. The explicit expressions used are as follows.

i. Radial Couplings

$$[\underline{P}^g]^R_{jn} = -i\hbar \langle\phi_j|(\partial V_e/\partial R)_{\vec{r}_g}|\phi_n\rangle/(\varepsilon_n-\varepsilon_j), \tag{IV-5a}$$

$$[\underline{A}^g]^R_{jn} = (im/2\hbar)\ (\varepsilon_j-\varepsilon_n)\ \langle\phi_j|z_g f|\phi_n\rangle, \tag{IV-5b}$$

where ε_n are the Born-Oppenheimer electronic eigenvalues,

z_g is the component of $\vec{r}_g$ on the molecular axis, and V_e is the electronic potential energy. To obtain (IV-5a) from (II-62a), I have used the Hellmann-Feynman relation.

We need to express $(\partial V_e/\partial R)_{\vec{r}_g}$ in terms of prolate spheroidal co-ordinates (see figure 3). We find that

$$(\partial V_e/\partial R)_{\vec{r}_g} = (e^2/2)\ \{Z_A \cos\theta_A/r_A{}^2 - Z_B \cos\theta_B/r_B{}^2\}. \quad \text{(IV-6)}$$

But

$$\cos\theta_J = (\xi\eta - f_J)/(\xi - f_J\eta), \quad \text{(IV-7)}$$

where J is A or B, and $f_A = -1$, $f_B = +1$. Thus, we find

$$(R/2)^3(\xi^2-\eta^2)(\partial V_e/\partial R)_{\vec{r}_g} = (Re^2/4)\ \{Z_A[\eta(\xi^2-1)+\xi(1-\eta^2)]/(\xi+\eta)^2 - Z_B[\eta(\xi^2-1)-\xi(1-\eta^2)]/(\xi-\eta)^2\}. \quad \text{(IV-8)}$$

ii. Angular Couplings

$$[\underline{P}^g]^\theta_{jn} = -\ R^{-1}\ \langle\phi_j|\hat{L}_y{}^g|\phi_n\rangle, \quad \text{(IV-9a)}$$

$$[\underline{A}^g]^\theta_{jn} = (im/2\hbar)\ (\varepsilon_j-\varepsilon_n)\ \langle\phi_j|x_g f|\phi_n\rangle, \quad \text{(IV-9b)}$$

where x_g is the component of $\vec{r}_g$ perpendicular to the molecular axis, and $\hat{L}_y{}^g$ is the y-component of the electronic orbital angular momentum, with respect to the geometric centre. Now

$$\hat{L}_y^g = -(i/2)(\hat{L}_+^g - \hat{L}_-^g), \qquad \text{(IV-10a)}$$

where $\hat{L}_\pm^g$ are the ladder operators raising and lowering the mol[illegible]ponent of orbital angular momentum;

$$\hat{L}_\pm^g = \hbar \exp(\pm i\phi)\,\{\pm\partial/\partial\theta + i \cot\theta\ \partial/\partial\phi\}. \qquad \text{(IV-10b)}$$

Using the relations,

$$r_g\cos\theta = (R/2)\xi\eta; \quad r_g\sin\theta = (R/2)(\xi^2-1)^{\frac{1}{2}}(1-\eta^2)^{\frac{1}{2}},$$

it can be shown that

$$\hat{L}_\pm^g = \hbar \exp(\pm i\phi)\ \{\pm[(\xi^2-1)^{\frac{1}{2}}(1-\eta^2)^{\frac{1}{2}}(\eta\partial/\partial\xi-\xi\partial/\partial\eta)/(\xi^2-\eta^2)]$$

$$+\ i\ \xi\eta/[(\xi^2-1)^{\frac{1}{2}}(1-\eta^2)^{\frac{1}{2}}]\ \partial/\partial\phi\}. \qquad \text{(IV-11)}$$

Computation of matrix elements reduces to separate quadratures over η, the "angle" variable, and ξ, the "radial" variable. The η-integrals were performed either analytically, or by 32-point Gauss-Legendre quadrature, whichever was more convenient; and the ξ-integrals were done by a 28-point truncation of the 64-point Gauss-

Laguerre quadrature formula.[48] All integrals are straightforward, except for those of $(\partial V_e/\partial R)\frac{+}{r_g}$, where a logarithmic singularity must be extracted analytically. I will describe the details of the matrix element computations in the next three sections. Unless the calculation of integrals holds a particular fascination for the reader, I suggest that he pass on quickly to the summary given in section F.

For those still with me, I will first establish the notation. To avoid confus[illegible]ial and final electronic states, this is slightly different from that [illegible] chapter III.

i. Bound States

$$|\phi_n\rangle = S_{\Gamma m}(\eta)\ X_{n\Gamma m}(\xi)\ \Phi_m(\phi), \tag{IV-12}$$

where n and Γ are the united-atom-limit, principal and angular momentum quantum numbers, respectively, and m is the modulus of the azimuthal quantum number.

$$S_{\Gamma m}(\eta) = \sum_{L=m} d_L^{\Gamma m}\ P_L^{m}(\eta), \tag{IV-13a}$$

$$X_{n\Gamma m}(\xi) = \exp(-c_n \xi)\ F_{n\Gamma m}(\xi), \tag{IV-13b}$$

where c_n is the eigenparameter, $c_n^2 = -\frac{1}{4}\,\varepsilon_n\,R^2$.

ii. Continuum States

$$\langle\phi_j| = S_{\Gamma'm'}(\eta)\; X^{reg}_{\varepsilon'\Gamma'm'}(\xi)\; \Phi^{*}_{m'}(\phi). \qquad \text{(IV-14)}$$

Γ' and m' have the same meaning as the corresponding unprimed parameters, and ε' is the continuum electronic energy.

$$S_{\Gamma'm'}(\eta) = \sum_{L=m'} d_L^{\Gamma'm'}\, P_L^{m'}(\eta), \qquad \text{(IV-15a)}$$

$$X^{reg}_{\varepsilon'\Gamma'm'}(\xi) = [(\xi-1)/(\xi+1)]^{m/2}\, F^{reg}_{\varepsilon'\Gamma'm'}(\xi). \qquad \text{(IV-15b)}$$

I will assume that both the bound and continuum states have been appropriately normalised.

C. Computation of the Matrix Elements of L_y

1. Introduction

The operators, $\hat{L}_{\pm}^{g}$, link states with m' = m±1, and the integration over ϕ can be done by inspection. Thus, in effect, the operator is

$$\hat{L}_{\pm}^{g} = \hbar\,(\pm\partial/\partial\theta - m\cot\theta). \qquad \text{(IV-16)}$$

All the integrals over η can be performed analytically, with the help of the recursion relations satisfied by the $P_L^{m}(\eta)$'s, and integration by parts. When $\langle\phi_j|$ is a continuum state, the ξ-integrals are all of the form

$$I(c_n) = \int_1^\infty \exp(-c_n\xi)\; g(\xi)\; d\xi \qquad \text{(IV-17a)}$$

$$\approx \exp(-c_n)/c_n \sum_i w_i\; g(\xi_i) \qquad \text{(IV-17b)}$$

$$\xi_i = 1 + x_i/c_n,$$

where x_i and w_i are the Gauss-Laguerre quadrature points and weights.

I will give the results for initial states with m = 0 (σ states), and m = 1 (π states).

2. $I^{+}_{\sigma\to\pi} = \langle\epsilon'\Gamma'\pi|\hat{L}_{+}^{g}|n\Gamma\sigma\rangle$ (m=0, m'=1)

From equation (IV-11),

$$I^{+}_{\sigma\to\pi} = \hbar\; (R/2)^3 \int_1^\infty X^{reg}_{\epsilon'\Gamma'\pi}(\xi)\; (\xi^2-1)^{1/2}\; \{\alpha(\sigma\to\pi)\; d/d\xi$$

$$-\; \beta(\sigma\to\pi)\,\xi\}\; X_{n\Gamma\sigma}(\xi)\; d\xi, \qquad \text{(IV-18a)}$$

where

$$\alpha(\sigma\to\pi) = \int_{-1}^{+1} S_{\Gamma'\pi}(\eta)\; (1-\eta^2)^{1/2}\; \eta\; S_{\Gamma\sigma}(\eta)\; d\eta \qquad \text{(IV-18b)}$$

$$= (6/5)\; d_2^{\Gamma'\pi} d_0^{\Gamma\sigma} + \sum_{L=1} 2(L+1)/[(2L+1)(2L+3)]$$

$$\{d_L^{\Gamma'\pi} d_L^{\Gamma\sigma}\; L/(2L-1) + (L+2)/(2L+5)\; [(L+3)\; d_{L+2}^{\Gamma'\pi} d_L^{\Gamma\sigma}$$

$$- L\ d_L^{\Gamma'\pi} d_{L+2}^{\Gamma\sigma}]\},$$

and

$$\beta(\sigma\to\pi) = \int_{-1}^{+1} S_{\Gamma'\pi}(\eta)\ (1-\eta^2)^{\frac{1}{2}}\ dS_{\Gamma\sigma}(\eta)/d\eta\ d\eta \qquad \text{(IV-18c)}$$

$$= \sum_{L=1} d_L^{\Gamma'\pi} d_L^{\Gamma\sigma}\ 2L(L+1)/(2L+1).$$

Hence,

$$I^{+}_{\sigma\to\pi} = \hbar\ (R/2)^3 \int_1^{\infty} \exp(-c_n\xi)\ \chi^{reg}_{\varepsilon'\Gamma'\pi}(\xi)\ (\xi^2-1)^{\frac{1}{2}}$$

$$\{\alpha\ dF_{n\Gamma\sigma}(\xi)/d\xi - (\alpha c_n+\beta\xi)\ F_{n\Gamma\sigma}(\xi)\}\ d\xi. \qquad \text{(IV-19)}$$

3. $I^{\mathcal{G}-}_{\pi\to\sigma} = \langle\varepsilon'\Gamma'\sigma|\hat{L}_-{}^g|n\Gamma\pi\rangle$ (m=1, m'=0)

If we notice that

$$\xi\eta(\xi^2-\eta^2)/[(\xi^2-1)^{\frac{1}{2}}(1-\eta^2)^{\frac{1}{2}}] = \xi(\xi^2-1)^{\frac{1}{2}}\eta/(1-\eta^2)^{\frac{1}{2}} +$$

$$\eta(1-\eta^2)^{\frac{1}{2}}\xi/(\xi^2-1)^{\frac{1}{2}},$$

then, for m = 1, after integration over ϕ,

$$(\xi^2-\eta^2)\ \hat{L}_{\pm}{}^g = \hbar\ \{[\pm(\xi^2-1)^{\frac{1}{2}}\partial/\partial\xi - \xi/(\xi^2-1)^{\frac{1}{2}}]\eta(1-\eta^2)^{\frac{1}{2}} -$$

$$[\pm(1-\eta^2)^{\frac{1}{2}}\partial/\partial\eta + \eta/(1-\eta^2)^{\frac{1}{2}}]\xi(\xi^2-1)^{\frac{1}{2}}\}. \qquad \text{(IV-20)}$$

After some manipulation, we obtain

$$I^-_{\pi\to\sigma} = - \hbar \; (R/2)^3 \int_1^\infty X^{reg}_{\varepsilon'\Gamma'\sigma}(\xi) \; \{\alpha(\pi\to\sigma) \; d/d\xi \; (\xi^2-1)^{\frac{1}{2}} +$$

$$\beta(\pi\to\sigma) \; \xi \; (\xi^2-1)^{\frac{1}{2}}\} \; X_{n\Gamma\pi}(\xi) \; d\xi, \qquad \text{(IV-21a)}$$

where (cf. equation (IV-18b))

$$\alpha(\pi\to\sigma) = (6/5) \; d_0^{\Gamma'\sigma} d_2^{\Gamma\pi} + \sum_{L=1} \; 2(L+1)/[(2L+1)(2L+3)]$$

$$\{d_L^{\Gamma'\sigma} d_L^{\Gamma\pi} \; L/(2L-1) + (L+2)/(2L+5) \; [(L+3) \; d_L^{\Gamma'\sigma} d_{L+2}^{\Gamma\pi} -$$

$$L \; d_{L+2}^{\Gamma'\sigma} d_L^{\Gamma\pi}]\}; \qquad \text{(IV-21b)}$$

and

$$\beta(\pi\to\sigma) = \sum_{L=1} \; d_L^{\Gamma'\sigma} d_L^{\Gamma\pi} \; 2L(L+1)/(2L+1). \qquad \text{(IV-21c)}$$

Hence,

$$I^-_{\pi\to\sigma} = - \hbar \; (R/2)^3 \int_1^\infty \exp(-c_n\xi) \; X^{reg}_{\varepsilon'\Gamma'\sigma}(\xi) \; \{\beta\xi - \alpha c_n + \alpha d/d\xi\}$$

$$(\xi^2-1)^{\frac{1}{2}} \; F_{n\Gamma\pi}(\xi) \; d\xi. \qquad \text{(IV-22)}$$

4. $I^+_{\pi\to\delta} = \langle\varepsilon'\Gamma'\delta|\hat{L}_+^g|n\Gamma\pi\rangle$ (m=1, m'=2)

From equation (IV-20), we see that

$$I^{+}_{\pi+\delta} = \hbar\ (R/2)^{3} \int_{1}^{\infty} X^{reg}_{\varepsilon'\Gamma'\delta}(\xi)\ \{\alpha(\pi+\delta)\,[(\xi^{2}-1)^{1/2}\ d/d\xi -$$

$$\xi/(\xi^{2}-1)^{1/2}] - \beta(\pi+\delta)\ \xi\,(\xi^{2}-1)^{1/2}\}\ X_{n\Gamma\pi}(\xi)\ d\xi, \quad \text{(IV-23a)}$$

where

$$\alpha(\pi+\delta) = \int_{-1}^{+1} S_{\Gamma'\delta}(\eta)\ \eta\ (1-\eta^{2})^{1/2}\ S_{\Gamma\pi}(\eta)\ d\eta$$

$$= (16/7)\ d_{3}^{\Gamma'\delta} d_{1}^{\Gamma\pi} + \sum_{L=2} 2L(L+1)(L+2)/[(2L+1)(2L+3)]$$

$$\{3d_{L}^{\Gamma'\delta} d_{L}^{\Gamma\pi}\ (L-1)/(2L-1) + (L+3)/(2L+5)\ [(L+4)\ d_{L+2}^{\Gamma'\delta} d_{L}^{\Gamma\pi} -$$

$$(L-1)\ d_{L}^{\Gamma'\delta} d_{L+2}^{\Gamma\pi}]\}; \quad \text{(IV-23b)}$$

and

$$\beta(\pi+\delta) = \int_{-1}^{+1} S_{\Gamma'\delta}(\eta)\ \{(1-\eta^{2})^{1/2}\ d/d\eta + \eta/(1-\eta^{2})^{1/2}\}\ S_{\Gamma\pi}(\eta)\ d\eta$$

$$= \sum_{L=2} d_{L}^{\Gamma'\delta} d_{L}^{\Gamma\pi}\ 2(L+2)(L+1)L(L-1)/(2L+1). \quad \text{(IV-23c)}$$

Therefore,

$$I^{+}_{\pi+\delta} = \hbar\ (R/2)^{3} \int_{1}^{\infty} \exp(-c_{n}\xi)\ X^{reg}_{\varepsilon'\Gamma'\delta}(\xi)\ \{(\xi^{2}-1)^{1/2}[\alpha d/d\xi - \alpha c_{n} -$$

$$\beta\xi] - \alpha\xi/(\xi^{2}-1)^{1/2}\}\ F_{n\Gamma\pi}(\xi)\ d\xi. \quad \text{(IV-24)}$$

This completes the calculation of the matrix elements of $\hat{L}_{\pm}^{g}$. The angular component of $\vec{\underline{P}}(R)$ is then given by

$$[P^{g}]^{\theta}_{jn} = \pm\ (i/2R)\ I^{\pm}_{m\to m'}. \tag{IV-25}$$

We now turn to the matrix elements of $(\partial V_e/\partial R)_{\vec{r}_g}$.

D. Matrix Elements of $(\partial/\partial R)_{\vec{r}_g}$

1. Introduction

We have to evaluate

$$I_{m\to m'} = \langle \varepsilon'\Gamma'm' | (\partial V_e/\partial R)_{\vec{r}_g} | n\Gamma m\rangle, \tag{IV-26}$$

where $(\partial V_e/\partial R)_{\vec{r}_g}$ is given by equation (IV-8). The integral over ϕ is trivial and yields the selection rule that the matrix elements are non-zero if, and only if, $m' = m$. Therefore,

$$I_m = (Re^2/4) \int_1^\infty X^{reg}_{\varepsilon'\Gamma'm}(\xi)\ X_{n\Gamma m}(\xi)\ \{Z_A\ I_+(\xi) - Z_B\ I_-(\xi)\}\ d\xi, \tag{IV-27a}$$

where

$$I_{\pm}(\xi) = \pm \int_{-1}^{+1} \{\xi(1-\eta^2) \mp \eta(\xi^2-1)\}/(\xi\pm\eta)^2\ S_{\Gamma'm}(\eta)\ S_{\Gamma m}(\eta)\ d\eta. \tag{IV-27b}$$

If we factor $S_{\Gamma'm}(\eta)$ and $S_{\Gamma m}(\eta)$ into even and odd parts,

$$S(\eta) = S^{e}(\eta) + S^{o}(\eta),$$

we find that

$$I_{\pm}(\xi) = \pm \int_{-1}^{+1} \{\xi(1-\eta^2)-\eta(\xi^2-1)\}/(\xi-\eta)^2 \; \{S^e_{\Gamma' m}(\eta) \mp S^o_{\Gamma' m}(\eta)\}$$

$$\{S^e_{\Gamma m}(\eta) \mp S^o_{\Gamma m}(\eta)\}\, d\eta. \qquad \text{(IV-28)}$$

Hence,

$$I_m'(\xi) = R\, \{Z_A\, I_+(\xi) - Z_B\, I_-(\xi)\}$$

$$= \int_{-1}^{+1} \{\xi(1-\eta^2)-\eta(\xi^2-1)\}/(\xi-\eta)^2 \; \{q(S^e_{\Gamma' m}S^e_{\Gamma m}+S^o_{\Gamma' m}S^o_{\Gamma m}) +$$

$$p(S^o_{\Gamma' m}S^e_{\Gamma m}+S^e_{\Gamma' m}S^o_{\Gamma m})\}\, d\eta; \qquad \text{(IV-29a)}$$

where

$$q = R(Z_B+Z_A), \qquad p = R(Z_B-Z_A). \qquad \text{(IV-29b)}$$

Thus, we have to compute

$$I_m = (e^2/4) \int_1^{\infty} X^{reg}_{\varepsilon' \Gamma' m}(\xi)\; X_{n\Gamma m}(\xi)\; I_m'(\xi)\, d\xi. \qquad \text{(IV-29c)}$$

The integrals, (IV-29), are not trivial, and it is instructive to examine their general behaviour, by looking at simpler integrals which have similar properties.

2. Model Problem

Consider the integral

$$\hat{I}(\xi) = \int_{-1}^{+1} \{\xi(1-\eta^2)-\eta(\xi^2-1)\}/(\xi-\eta)^2 \, P_L(\eta) \, d\eta . \qquad \text{(IV-30)}$$

If we use the fact that

$$Q_n(x) = \tfrac{1}{2} \int_{-1}^{+1} P_n(y)/(x-y) \, dy, \qquad \text{(IV-31a)}$$

where $Q_n(x)$ is the n'th Legendre function of the second kind, it can be shown that

$$\hat{I}(\xi) = 2/(2L+1) \, \{(L+1)(L+2) \, Q_{L+2}(\xi) - L(L-1) \, Q_{L-2}(\xi)\} - (2/3) \, \delta_{L,1} . \qquad \text{(IV-31b)}$$

But

$$Q_n(x) = \tfrac{1}{2} P_n(x) \ln\{(x+1)/(x-1)\} - W_{n-1}(x),$$

i.e., $Q_n(x)$ has a logarithmic singularity at $x = 1$. In general, numerical integration schemes are inaccurate when such behaviour is present, and one has to extract the singularity analytically. To illustrate the principle, let us consider integrals of the type

$$\tilde{I} = \int_1^\infty e^{-x}\, f(x)\, \{\int_{-1}^{+1} g(y)/(x-y)\, dy\}\, dx, \qquad \text{(IV-32a)}$$

where f(x) and g(y) are well-behaved functions, for which Taylor expansions about unity are known:

$$F(x) = a_1 + a_2(x-1) + a_3(x-1)^2 \simeq f(x), \qquad \text{(IV-32b)}$$

$$G(y) = b_1 + b_2(1-y) + b_3(1-y)^2 \simeq g(y). \qquad \text{(IV-32c)}$$

Using functions, f(x) and g(y), for which $\tilde{I}$ can be evaluated analytically, extensive calculations showed that the following procedure works extremely well.

i. Evaluate

$$I_1(x) = \int_{-1}^{+1} \{g(y)-G(y)\}/(x-y)\, dy \qquad \text{(IV-33a)}$$

numerically, by 32-point Gauss-Legendre quadrature.[48] This yields

$$I_1(x) \simeq \sum_{i=1}^{16} w_i' \, [\{g(y_i)-G(y_i)\}/(x-y_i) +$$

$$\{g(-y_i)-G(-y_i)\}/(x+y_i)], \qquad \text{(IV-33b)}$$

where w_i' and y_i are the Gauss-Legendre quadrature weights and points. Near x = 1, $I_1(x)$ behaves like $(x-1)^3 \ln\{(x+1)/(x-1)\}$, and, at large x, like 1/x.

ii. Evaluate

$$I_2(x) = \int_{-1}^{+1} G(y)/(x-y)\ dy \qquad \text{(IV-34)}$$

$$= b_1 \ln\{(x+1)/(x-1)\} - b_2 \,[(x-1) \ln\{(x+1)/(x-1)\} - 2]$$

$$+ b_3 \,[(x-1)^2 \ln\{(x+1)/(x-1)\} - 2(x-1) + 2]$$

$$= 2\,\{b_1 Q_0 - b_2(Q_1-Q_0) + (2b_3/3)(Q_2-3Q_1+2Q_0)\}.$$

iii. We now have

$$\tilde{I} = \int_1^\infty e^{-x}\, f(x)\ \{I_1(x)+I_2(x)\}\ dx \qquad \text{(IV-35)}$$

$$= \int_1^\infty e^{-x}\ \{f(x)\ I_1(x) + [f(x)-F(x)]\ I_2(x)\}\ dx +$$

$$\int_1^\infty e^{-x}\ F(x)\ I_2(x)\ dx.$$

iv. Evaluate

$$I_3 = \int_1^\infty e^{-x}\ \{f(x)\ I'_1(x) + [f(x)-F(x)]\ I_2(x)\}\ dx \qquad \text{(IV-36)}$$

by Gauss-Laguerre quadrature.[48] Near x = 1, the term in braces behaves like a polynomial plus $(x-1)^3 \ln\{(x+1)/(x-1)\}$, and the numerical integration is very accurate.

v. Finally, we need

$$I_4 = \int_1^\infty e^{-x} F(x)\ I_2(x)\ dx. \qquad \text{(IV-37)}$$

The problem here is the logarithmic singularity at x = 1. Direct application of the Gauss-Laguerre integration formula gives very low accuracy. However, it is possible to use a variation of this technique, as follows. Consider

$$I^n = \int_0^\infty e^{-x} x^n\ dx = \sum_{j=1}^{N} w_j\ x_j^{\ n}, \qquad \text{(IV-38)}$$

where x_j and w_j are the quadrature points and weights. If n<N, the sum is exactly I^n. Now set

$$x = -\ln(t), \qquad dt = -\ e^{-x}\ dx.$$

Equation (IV-38) then becomes

$$I^n = \int_0^1 \{-\ln(t)\}^n\ dt = \sum_{j=1}^{N} w_j\ \{-\ln(t)\}^n. \qquad \text{(IV-39)}$$

Again, for n<N, the sum is exactly I^n, and this gives us a method of evaluating I_4. Write

$$I_4 = \int_1^2 e^{-x}\ F(x)\ I_2(x)\ dx + \int_2^\infty e^{-x}\ F(x)\ I_2(x)\ dx \qquad \text{(IV-40a)}$$

$$\simeq \sum_i w_i \{F(t_i)\, I_2(t_i) \exp(-t_i) + F(z_i)\, I_2(z_i)\, e^{-2}\},$$

where

$$t_i = 1 + \exp(-x_i), \qquad z_i = 2 + x_i. \qquad \text{(IV-40b)}$$

We now return to the problem of computing the matrix elements of $(\partial V_e/\partial R)_{\vec{r}_g}$. As in the model problem, the basic idea is to isolate terms up to and including those which behave like $(\xi-1)^2 \ln\{(\xi+1)/(\xi-1)\}$, by means of Taylor expansions about $\xi = \eta = 1$.

3. $I_\sigma = \langle \varepsilon'\Gamma'\sigma | (\partial V_e/\partial R)_{\vec{r}_g} | n\Gamma\sigma\rangle$ $(m=m'=0)$

a. η-integrals

Near $\eta = I$, expand $S_{\Gamma'\sigma}(\eta)\, S_{\Gamma\sigma}(\eta)$ as a power series in $(1-\eta)$. Now

$$P_K^{\,0}(\eta)\, P_L^{\,0}(\eta) \simeq a_\sigma + b_\sigma(1-\eta) + c_\sigma(1-\eta)^2, \qquad \text{(IV-41a)}$$

where

$$a_\sigma = 1, \qquad b_\sigma = -\tfrac{1}{2}\{K(K+1)+L(L+1)\}, \qquad \text{(IV-41b)}$$

$$c_\sigma = (1/16)\,\{(K-1)K(K+1)(K+2) + 4K(K+1)L(L+1) + (L-1)L(L+1)(L+2)\}. \qquad \text{(IV-41c)}$$

Using these relations, it is a simple, if tedious, matter to write (cf. equation (IV-29))

$$q(S^e_{\Gamma'\sigma}S^e_{\Gamma\sigma}+S^o_{\Gamma'\sigma}S^o_{\Gamma\sigma}) + p(S^o_{\Gamma'\sigma}S^e_{\Gamma\sigma}+S^e_{\Gamma'\sigma}S^o_{\Gamma\sigma})$$

$$= XE_\sigma(\eta) + XO_\sigma(\eta) \qquad \text{(IV-42)}$$

$$\simeq A_\sigma + B_\sigma(1-\eta) + C_\sigma(1-\eta)^2.$$

From equations (IV-30) and (IV-31), it can be shown that

$$I^{anal}_\sigma(\xi) = \int_{-1}^{+1}\{\xi(1-\eta^2)-\eta(\xi^2-1)\}/(\xi-\eta)^2\ \{A_\sigma+B_\sigma(1-\eta)+ C_\sigma(1-\eta)^2\}\ d\eta \qquad \text{(IV-43)}$$

$$= 4\ \{A_\sigma Q_2 + B_\sigma(Q_2-Q_3) + (2C_\sigma/15)(6Q_4-15Q_3+10Q_2- Q_0)\} + (2/3)(B_\sigma+2C_\sigma).$$

Therefore, $I_\sigma'(\xi)$ in equation (IV-29) is given by

$$I_\sigma'(\xi) = \int_{-1}^{+1}\{\xi(1-\eta^2)-\eta(\xi^2-1)\}/(\xi-\eta)^2\ \{XE_\sigma(\eta)+XO_\sigma(\eta)\}\ d\eta$$

$$= I^{anal}_\sigma(\xi) + \int_{-1}^{+1}\{\xi(1-\eta^2)-\eta(\xi^2-1)\}/(\xi-\eta)^2\ \{XE_\sigma(\eta)+ XO_\sigma(\eta)-A_\sigma-B_\sigma(1-\eta)-C_\sigma(1-\eta)^2\}\ d\eta. \qquad \text{(IV-44)}$$

The leading logarithmic term in the second integral behaves like $(\xi-1)^3 \ln\{(\xi+1)/(\xi-1)\}$ near $\xi=1$, and I used Gauss-Legendre numerical integration to evaluate this integral as a function of ξ; call the result $I_\sigma^{num}(\xi)$. The $P_L^m(\eta)$'s can be calculated from their recursion relation.[55]

b. <u>ξ-integrals</u>

Equation (IV-29c) now becomes

$$I_\sigma = (e^2/4) \int_1^\infty X^{reg}_{\varepsilon'\Gamma'\sigma}(\xi)\, X_{n\Gamma\sigma}(\xi)\, \{I_\sigma^{anal}(\xi)+I_\sigma^{num}(\xi)\}\, d\xi. \tag{IV-45}$$

Near =1,

$$X^{reg}_{\varepsilon'\Gamma'\sigma}(\xi)\, X_{n\Gamma\sigma}(\xi) \approx \exp(-c_n\xi)\, (\xi+1)^{q/2c_n-1}\, \{\alpha_\sigma+\beta_\sigma(\xi-1)+ \gamma_\sigma(\xi-1)^2\}, \tag{IV-46a}$$

where

$$\alpha_\sigma = a_0 b_0, \qquad \beta_\sigma = a_1 b_0 + \tfrac{1}{2} a_0 b_1, \tag{IV-46b}$$

$$\gamma_\sigma = \tfrac{1}{2} \{2a_2 b_0 + a_1 b_1 + \tfrac{1}{2} a_0 (b_2-b_1)\}; \tag{IV-46c}$$

and a_i, b_i are the leading terms in the expansions, (III-38) (continuum states), and (III-17) (bound states), respectively. Therefore,

$$I_\sigma = (e^2/4) \int_1^\infty \exp(-c_n\xi) \{X^{reg}_{\varepsilon'\Gamma'\sigma}(\xi)\ F_{n\Gamma\sigma}(\xi)\ I^{num}_\sigma(\xi) + (X^{reg}_{\varepsilon'\Gamma'\sigma}(\xi)\ F_{n\Gamma\sigma}(\xi) - (\xi+1)^{q/2c_n-1}\ [\alpha_\sigma+\beta_\sigma(\xi-1)+\gamma_\sigma(\xi-1)^2])\ I^{anal}_\sigma(\xi)\}\ d\xi + (e^2/4) \int_1^\infty \exp(-c_n\xi)\ (\xi+1)^{q/2c_n-1}\ \{\alpha_\sigma + \beta_\sigma(\xi-1)+\gamma_\sigma(\xi-1)^2\}\ I^{anal}_\sigma(\xi)\ d\xi. \tag{IV-47}$$

As in the model problem, the first integral can be performed accurately by Gauss-Laguerre quadrature; and the second is evaluated in two parts: from 1 to 2, and from 2 to ∞ (see equations (IV-35) to (IV-40)). The $Q_n(\xi)$'s are computed using the explicit expressions near $\xi=1$, and the power series at larger ξ-values.[55]

4. $I_\pi = \langle\varepsilon'\Gamma'\pi|(\partial V_e/\partial R)_{\vec{r}_g}|n\Gamma\pi\rangle$ $(m'=m=1)$

a. η-integrals

We follow exactly the same procedure as in section 3 above. Near $\eta = 1$,

$$P_K{}^1(\eta)\ P_L{}^1(\eta) \simeq (1-\eta)\ \{a_\pi + b_\pi(1-\eta)\}, \tag{IV-48a}$$

where

$$a_\pi = \tfrac{1}{2}\ K(K+1)L(L+1), \tag{IV-48b}$$

$$b_\pi = -\tfrac{1}{4}\ a_\pi\ \{K(K+1) + L(L+1) - 2\}. \tag{IV-48c}$$

Using the above relations, we can expand the product of the angular eigenfunctions as a power series in (1-η):

$$q(S^{e}_{\Gamma'\pi}S^{e}_{\Gamma\pi}+S^{o}_{\Gamma'\pi}S^{o}_{\Gamma\pi}) + p(S^{o}_{\Gamma'\pi}S^{e}_{\Gamma\pi}+S^{e}_{\Gamma'\pi}S^{o}_{\Gamma\pi})$$

$$= XE_{\pi}(\eta) + XO_{\pi}(\eta) \qquad \text{(IV-49)}$$

$$\simeq (1-\eta)\ \{A_{\pi}+B_{\pi}(1-\eta)\}.$$

From equations (IV-30) and (IV-31),

$$I^{anal}_{\pi}(\xi) = \int_{-1}^{+1} \{\xi(1-\eta^2)-\eta(\xi^2-1)\}/(\xi-\eta)^2\ \{A_{\pi}(1-\eta)+ B_{\pi}(1-\eta)^2\}\ d\eta \qquad \text{(IV-50)}$$

$$= 4\ \{A_{\pi}(Q_2-Q_3) + (2B_{\pi}/15)(6Q_4-15Q_3+10Q_2-Q_0)\} + (2/3)(A_{\pi}+2B_{\pi});$$

and

$$I^{num}_{\pi}(\xi) = \int_{-1}^{+1} \{\xi(1-\eta^2)-\eta(\xi^2-1)\}/(\xi-\eta)^2\ \{XE_{\pi}(\eta)+XO_{\pi}(\eta)- A_{\pi}(1-\eta)-B_{\pi}(1-\eta)^2\}\ d\eta$$

$$= \int_{-1}^{+1} H(\eta)\ d\eta \simeq \sum_{i=1}^{16} w_i'\ \{H(\eta_i)+H(-\eta_i)\}, \qquad \text{(IV-51)}$$

where η_i, w_i' are the Gauss-Legendre quadrature points and weights.

b. ξ-integrals

$$I_\pi = (e^2/4) \int_1^\infty \exp(-c_n\xi)\, X^{reg}_{\varepsilon'\Gamma'\pi}(\xi)\, F_{n\Gamma\pi}(\xi)\, \{I^{anal}_\pi(\xi) + I^{num}_\pi(\xi)\}\, d\xi. \qquad \text{(IV-52)}$$

Near $\xi = 1$,

$$X^{reg}_{\varepsilon'\Gamma'\pi}(\xi)\, F_{n\Gamma\pi}(\xi) \simeq (\xi-1)(\xi+1)^{q/2c_n-2}\{\alpha_\pi+\beta_\pi(\xi-1)\}, \qquad \text{(IV-53a)}$$

where

$$\alpha_\pi = a_0b_0, \qquad \beta_\pi = a_1b_0 + \tfrac{1}{2}\, a_0b_1; \qquad \text{(IV-53b)}$$

and a_i, b_i are the leading terms in the expansions, (III-38) (continuum states), and (III-17) (bound states), respectively. Therefore,

$$I_\pi = (e^2/4) \int_1^\infty \exp(-c_n\xi)\{X^{reg}_{\varepsilon'\Gamma'\pi}(\xi)\, F_{n\Gamma\pi}(\xi)\, I^{num}_\pi(\xi) + \left(X^{reg}_{\varepsilon'\Gamma'\pi}(\xi)\, F_{n\Gamma\pi}(\xi) - (\xi-1)(\xi+1)^{q/2c_n-2}\, [\alpha_\pi+\beta_\pi(\xi-1)]\right) I^{anal}_\pi(\xi)\}\, d\xi + (e^2/4) \int_1^\infty \exp(-c_n\xi)\, (\xi-1)(\xi+1)^{q/2c_n-2}\, \{\alpha_\pi + \beta_\pi(\xi-1)\}\, I^{anal}_\pi(\xi)\, d\xi. \qquad \text{(IV-54)}$$

These integrals are computed exactly as in the I_σ case.

This completes the calculation of the matrix elements of $(\partial V_e/\partial R)_{\vec{r}_g}$. The radial component of $\vec{P}(R)$ is then given by

$$[P^g]^R_{jn} = (-i\hbar)\, I_m/(\varepsilon_n - \varepsilon_j). \qquad \text{(IV-55)}$$

We now turn to the matrix elements of $\vec{s}^g$.

E. Matrix Elements of $[h_{BO}, \vec{s}^g]$

1. Introduction

We have to compute (see equations (IV-5b) and (IV-9b)):

i. $$I_m^R = \langle \varepsilon'\Gamma'm | z_g f | n\Gamma m\rangle \qquad \text{(IV-56a)}$$

$$z_g = (R/2)\,\xi\eta \qquad \text{(IV-56b)}$$

ii. $$I^\Theta_{m\to m'} = \langle \varepsilon'\Gamma'm' | x_g f | n\Gamma m\rangle \qquad \text{(IV-57a)}$$

$$x_g = (R/2)\ (\xi^2-1)^{1/2}(1-\eta^2)^{1/2}\cos\phi \qquad \text{(IV-57b)}$$

For the switching function, I propose to use the form (see figure 7):

$$f = \tanh(A\eta+B), \qquad \text{(IV-58)}$$

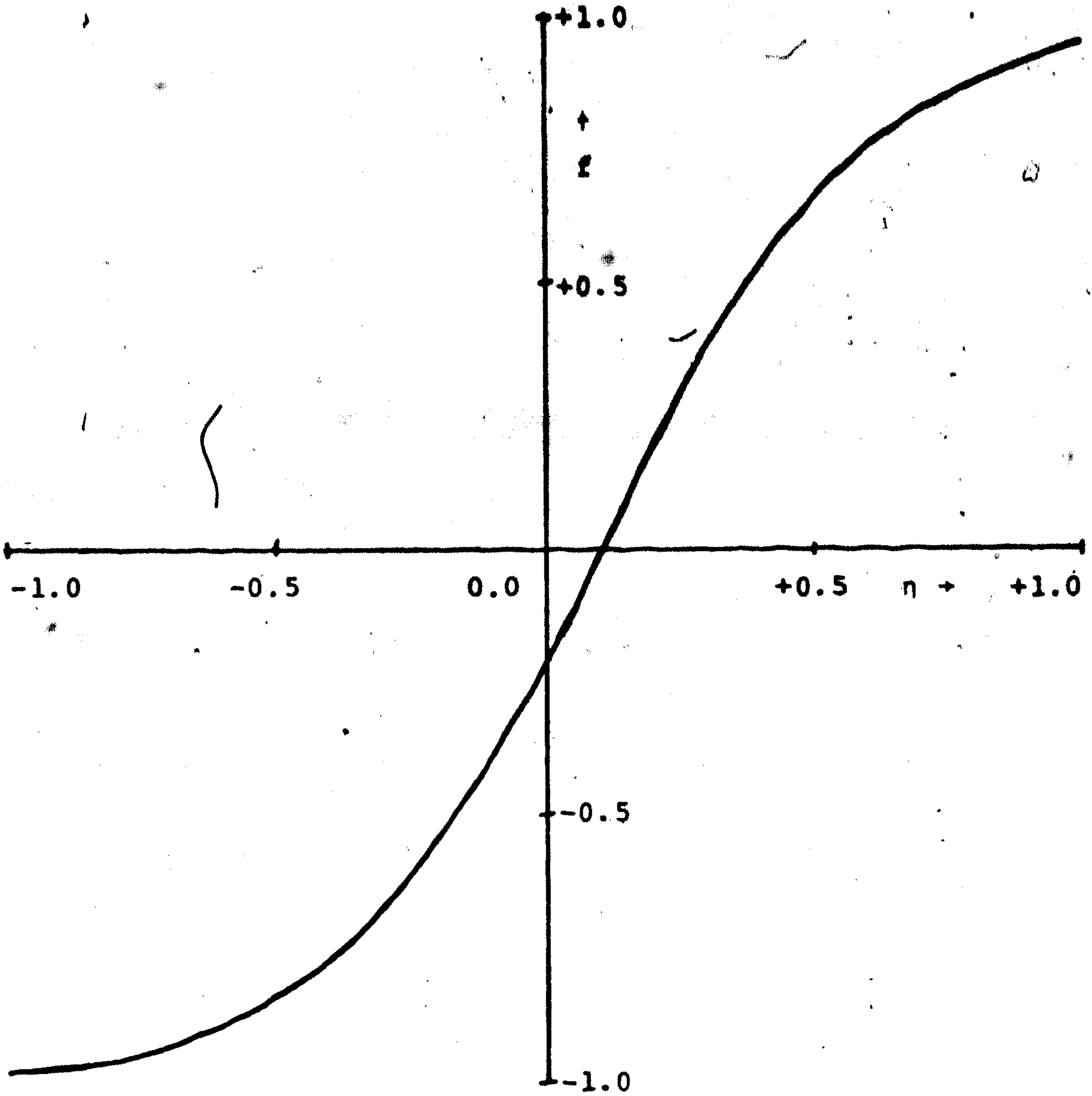

Figure 7. Model switching function: f = tanh(2η-0.2)

where the parameters, A and B, are to be determined. This will be discussed in detail in the next chapter.

The integrals over ϕ can be done by inspection, and yield the selection rules for m: matrix elements are non-zero only if $m' = m$, for the radial component; and $m' = m \pm 1$, for the angular component. Of course, these rules are the same as those for the matrix elements of $(\partial V_e/\partial R)_{\vec{r}_g}$ and $\hat{L}_\pm^g$, respectively. Both the η- and ξ-integrals are evaluated numerically, and they are quite straightforward.

2. Evaluation of I_m^R

$$I_m^R = (R/2)^4 \int_1^\infty \exp(-c_n\xi)\, X^{reg}_{\varepsilon'\Gamma'm}(\xi)\, F_{n\Gamma m}(\xi)\, \xi\, (\xi^2 I_1 - I_2)\, d\xi, \tag{IV-59a}$$

where

$$I_1 = \int_{-1}^{+1} S_{\Gamma' m}(\eta)\, S_{\Gamma m}(\eta)\, \eta\, \tanh(A\eta+B)\, d\eta, \tag{IV-59b}$$

$$I_2 = \int_{-1}^{+1} S_{\Gamma' m}(\eta)\, S_{\Gamma m}(\eta)\, \eta^3\, \tanh\,(A\eta+B)\, d\eta. \tag{IV-59c}$$

The integrals, I_1 and I_2, are evaluated by 32-point Gauss-Legendre quadrature. To simplify the expressions, write $\eta\, S_{\Gamma' m}(\eta)\, S_{\Gamma m}(\eta)$ as the sum of even and odd parts,

$$\eta\, S_{\Gamma' m}(\eta)\, S_{\Gamma m}(\eta) = SE(\eta) + SO(\eta), \tag{IV-60}$$

which can be calculated explicitly from equations (IV-13a) and (IV-15a). Therefore,

$$I_1 \simeq \sum_{j=1}^{16} w_j' \{[SE(\eta_j)+SO(\eta_j)] \tanh(A\eta_j+B) - [SE(\eta_j)-SO(\eta_j)] \tanh(-A\eta_j+B)\}; \qquad \text{(IV-61a)}$$

and

$$I_2 \simeq \sum_{j=1}^{16} w_j' \{[SE(\eta_j)+SO(\eta_j)] \tanh(A\eta_j+B) - [SE(\eta_j)-SO(\eta_j)] \tanh(-A\eta_j+B)\} \eta_j^2. \qquad \text{(IV-61b)}$$

The ξ-integrals are now evaluated by Gauss-Laguerre quadrature.

3. Evaluation of $I^{\Theta}_{m\to m'}$

$$I_{m\to m'} = \tfrac{1}{2} (R/2)^4 \int_1^\infty \exp(-c_n\xi)\, X^{reg}_{\epsilon'\Gamma'm'}(\xi)\, F_{n\Gamma m}(\xi)\, (\xi^2-1)^{\frac{1}{2}} (\xi^2 I_3 - I_4)\, d\xi, \qquad \text{(IV-62a)}$$

where

$$I_3 = \int_{-1}^{+1} S_{\Gamma'm'}(\eta)\, S_{\Gamma m}(\eta)\, (1-\eta^2)^{\frac{1}{2}} \tanh(A\eta+B)\, d\eta; \qquad \text{(IV-62b)}$$

and

$$I_4 = \int_{-1}^{+1} S_{\Gamma' m'}(\eta)\ S_{\Gamma m}(\eta)\ (1-\eta^2)^{\frac{1}{2}} \tanh(A\eta+B)\ \eta^2\ d\eta. \tag{IV-62c}$$

The factor of $\frac{1}{2}$ comes from the integration over ϕ. Now[55]

$$(1-\eta^2)^{\frac{1}{2}}\ P_L{}^m(\eta) = (2L+1)^{-1}\ \{P_{L+1}^{m+1}(\eta) - P_{L-1}^{m+1}(\eta)\},$$

and this relation can be used to simplify the integrals, so that they only involve one set of $P_L{}^m(\eta)$'s. If $m' = m + 1$, use the relation to express $(1-\eta^2)^{\frac{1}{2}}\ S_{\Gamma m}(\eta)$ as a sum of $P_L{}^{m'}(\eta)$'s; on the other hand, if $m' = m - 1$, use it to express $(1-\eta^2)^{\frac{1}{2}}\ S_{\Gamma' m'}(\eta)$ as a sum of $P_L{}^m(\eta)$'s. In either case, write $(1-\eta^2)^{\frac{1}{2}}\ S_{\Gamma' m'}(\eta)\ S_{\Gamma m}(\eta)$ as a sum of even and odd parts:

$$(1-\eta^2)^{\frac{1}{2}}\ S_{\Gamma' m'}(\eta)\ S_{\Gamma m}(\eta) = YE(\eta) + YO(\eta). \tag{IV-63}$$

Thus, I_3 and I_4 reduce to exactly the same forms as I_1 (equation (IV-59b)) and I_2 ((IV-59c)), and the evaluation of $I^{\Theta}_{m\to m'}$ proceeds on exactly the same lines as that of $I_m{}^R$.

The components of $\vec{\underline{A}}(R)$ are then given by

$$[A^g]^R_{jn} = (im/2\hbar)\ (\varepsilon_j - \varepsilon_n)\ I_m{}^R, \tag{IV-64a}$$

$$[A^g]^{\Theta}_{jn} = (im/2\hbar)\ (\varepsilon_j - \varepsilon_n)\ I^{\Theta}_{m\to m'}. \tag{IV-64b}$$

F. Summary

In this chapter, I have described the evaluation of the matrix elements af $\vec{\underline{P}}(R) + \vec{\underline{A}}(R)$ in great detail, for transitions from bound molecular states to the electronic continuum. For the next chapter, I would like the reader to imagine that we have a "black-box" computer programme. If we give the programme:

i. the nuclear charges, e.g., $Z_A = 2.0$, $Z_B = 1.0$

ii. bound state, united-atom-limit quantum numbers, e.g., $n = 2$, $\Gamma = 1$, $m = 0$ (2pσ state)

iii. continuum state energy (or energies), united-atom-limit angular momentum, and azimuthal quantum numbers, e.g., $\varepsilon' = 0.5$ Ry., $\Gamma' = 1(1)5$, $m' = 1$ (p, d, f, g, and h π-waves)

iv. the parameters, A and B, in the switching function

v. the desired range of R-values, e.g., 0.25(0.25)10.0

then the computer will calculate for us, at each R-value:

i. the bound state eigenenergy and separation constant

ii. the continuum state separation constant and phase shift

iii. $[P^g(R)]_{jn}$ and $[P^g(R)+A^g(R)]_{jn}$

In our example, it will calculate the angular couplings from the 2pσ state to the five partial waves specified. In the next chapter, I will discuss the variation of the matrix elements with the parameters, A and B. We will assume that the programme is debugged...

CHAPTER V

RESULTS

A. Introduction[56]

In earlier chapters, I have pointed out that non-adiabatic couplings between low-lying bound states and the electronic continuum are extremely sensitive to the choice of the switching function. Studies of this f-dependence may provide useful insight; and it may also be possible to choose an f which is in some sense "optimum" for a particular problem.

Such studies have been carried out by Thorson and coworkers,[2] in connection with the calculation of direct impact ionisation cross sections in H^+-H(1s) collisions. For each bound state they studied ($1s\sigma_g$, $2p\sigma_u$, $2p\pi_u$, in united atom notation), they found that a definite choice for the switching function may be made, which simultaneously and systematically reduces the couplings from that state to all continuum states, in most cases by several orders of magnitude. Whereas the uncorrected pss theory predicts large couplings to 30-40 continuum partial waves, with the envelope of these couplings having a range of about 40 au; the corrected couplings are significant only for the first two or three partial waves, and their range is less than 12 au. It was shown that the switching functions which achieve these spectacular reductions do not depend on the energy, or other quantum numbers, of the continuum states, nor upon the type of coupling causing transitions (radial or angular); however, the f's are different for each discrete state. From these results, one could infer that the switching functions so determined are characteristic of the discrete states themselves, and and might therefore be relevant to the computation of corrected couplings for transitions other than ionisation --for example, close coupling between discrete states. This possibility was an important motivation for the work reported in this chapter. I have extended the studies described in reference 2 to electrically asymmetric systems, such as HeH^{++}, and to additional discrete states; I have also made the procedure for selecting the switching function parameters more systematic. The corrected matrix elements reported here can also be used to calculate ionisation cross sections, for these more general systems.

The formulation of slow collision theory using switching functions can be extended so that each discrete electronic state, $|n\rangle$, has a translation factor with a different characteristic switching function, $f_n(\vec{r};\vec{R})$. This extension is quite straightforward at the level of a semiclassical approximation, and the main results are as follows (see Appendix).

i. The resulting close-coupled equations have the same form as those derived in chapter II, and the expression for the corrected nonadiabatic coupling matrix elements also has the same form (see equations (V-2) and (V-3), below)

ii. Since the switching functions, f_n, f_j, are different, the electronic states, $|n>$, $|j>$, are not orthogonal, and the corrected nonadiabatic couplings are not Hermitian; however, the non-Hermitian character exactly compensates for the non-orthogonality of the basis kets, and guarantees that the coupled equations conserve probability

iii. In the asymptotic channel limits, the electronic states are rigorously orthogonal, so vector solutions to the coupled equations give directly the unitary S-matrix for a collision, in the limit, $t \to +\infty$.

This establishes that a switching function formulation of a close-coupling slow collision problem, with a different switching function for each molecular state, provides a formally valid theory (provided, of course, that the f_n's satisfy the asymptotic constraints).

As I pointed out in chapter I, most earlier treatments of the slow collision problem, which correctly take account of boundary conditions and translation factors, can be recovered as special cases of this general formulation. In electrically asymmetric systems, the molecular states asymptotically correlate in a one-to-one fashion with atomic states of either nucleus A or B. If we choose $f_n = +1$ for the asymptotic B-states, and $f_n = -1$ for the A-states, the formulation of Bates and McCarroll[3] is obtained. This is also exactly equivalent to the formalism (based on projection operators) proposed by Matveyenko,[24] and is essentially equavalent to the "distorted cluster states" method of Y. Hahn.[23] For symmetric systems, the connection between a switching function approach and these other methods is not so clear.

In this chapter, I will describe the selection of a more elaborate set of switching functions for several discrete states of two-centre, one-electron systems. The states studied are the 1sσ, 2sσ, 2pσ, 2pπ, and 3dσ states (united atom notation); for systems with nuclear charges, $Z_B = +1.0$, $+1.0 \leq Z_A \leq +2.0$. The selection criterion is based on the remarkable sensitivity, of continuum couplings from these states, to the detailed form of the switching function, as reported earlier[2] for H_2^+. We find that there are very specific choices for each switching function, $f_n(\vec{r};\vec{R})$, which are independent of continuum state properties, or the type of coupling considered, but are characteristic of each discrete state, $|n$[illegible] As stated earlier, this approach suggests that these switching functions may be appropriate for problems more [illegible]al than the ionisation one.

These calculations are not based rigorously upon any formal variational principle, nor is the set of switching functions so obtained unique, or a "best," choice in any absolute sense. However, this set may have some advantages for close-coupling studies, and this point is discussed in section D, by some comparisons with alternative formulations.

In the rest of the Introduction, I will summarise the definitions of the coupling matrix elements. Section B describes the procedure used to select the switching function parameters; and section C presents the results of the calculations.

In uncorrected pss theory, the matrix elements for nonadiabatic coupling are defined

$$\vec{P}_{jn}(R) = -i\hbar \langle\phi_j|(\vec{\nabla}_R)_{\vec{r}}|\phi_n\rangle. \qquad \text{(V-1)}$$

In the corrected theory, $\vec{\underline{P}}(R)$ is simply replaced by $\vec{\underline{P}}^g(R) + \vec{\underline{A}}^g(R)$, where

$$\vec{P}^g_{jn}(R) = -i\hbar \langle\phi_j|(\vec{\nabla}_R)_{\vec{r}}|\phi_n\rangle; \qquad \text{(V-2)}$$

and

$$\vec{A}^g_{jn}(R) = (im/\hbar) \langle\phi_j|[h_{BO},\vec{s}_n{}^g]|\phi_n\rangle, \qquad \text{(V-3)}$$

with

$$\vec{s}_n^{\,g} = \tfrac{1}{2}\, f_n(\vec{r};\vec{R})\, \vec{r}_g. \qquad \text{(V-4)}$$

These equations are exactly equivalent to equations (IV-1) to (IV-4), with $f(\vec{r};\vec{R})$ replaced by $f_n(\vec{r};\vec{R})$ (see Appendix).

B. "Optimisation" Procedure

For their calculations on the H_2^+ system, Lebeda, Thorson, and Levy[2a] used a switching function of the form

$$f_n(\vec{r};\vec{R}) = \tanh\{\beta_n(R)R\eta\}, \qquad \text{(V-5)}$$

where $\beta_n(R)$ is a variable parameter. For each discrete state they studied, at a series of R-values, they plotted the magnitudes of the corrected radial coupling matrix elements against β, for a series of partial waves. At each R, they showed that there is a particular value, β_n, which produces spectacular reductions in the corrected couplings to higher partial waves, relative to the pss values. The same value of β_n was obtained by independent calculations at several different continuum energies. Similar calculations by SethuRaman, Thorson, and Lebeda[2b] for the angular couplings gave approximately the same values of β_n as were obtained for radial couplings.

I have repeated these calculations, and extended them to additional discrete states, and to electrically asymmetric systems; rather than determine $\beta_n(R)$ graphically, I have made the selection procedure automatic, and numerically more precise. However, the main idea, and the behaviour observed, are the same as in reference 2. Using a suitable parametric form for the switching function, we look for specific choices of the defining parameters which achieve large, *simultaneous* reductions in as many of the continuum couplings as possible, and we define as "optimum" the parameters which best achieve this. This idea is justified by the remarkable results obtained, rather than by any a priori arguments.

For a system with nuclear charges, Z_A, Z_B, at each R, and for each discrete state, $|n\rangle$, considered, the procedure that I used is as follows.

i. Consider a set of continuum states, $\{\langle j|\}$, with the same (arbitrary) energy, ε_j, and azimuthal quantum number, m'; and linked to $|n\rangle$ by either radial (m'=m), or angular (m'=m±1), coupling. The set, $\{\langle j|\}$, is thus a set of "partial waves" characterised by the "angular" eigenvalues, and I have indexed them by the corresponding united-atom-limit orbital angular momentum quantum number, L'.

ii. For each state, $\langle j|$, we define the *residuum*

$$\rho_{jn} = |1 + (A^g_{jn}/P^g_{jn})|, \qquad \text{(V-6)}$$

where the matrix elements are the radial (equation (IV-5)), or angular (equation (IV-9)), components of $\underline{\vec{P}}^g$ and $\underline{\vec{A}}^g$ (with f replaced by f_n). ρ_{jn} is just the magnitude of the corrected coupling, relative to the uncorrected (geometric centre) pss matrix element.

iii. The parametric form used for f_n is

$$f_n = \tanh\{R\left(\tfrac{1}{2}\beta_n[(Z_A+Z_B)\eta+(Z_A\ \ Z_B)] + \alpha_n \ln(Z_B/Z_A)\right)\} \quad \text{(V-7)}$$

where α_n and β_n are variable parameters. This reduces to the form (V-5), for $Z_B = Z_A$; it is equivalent to the form, $\tanh\{R(B_n\eta+A_n)\}$ (cf. equation (V-58)), but it displays more explicitly the observed charge dependence in the optimum switching functions.

iv. For each set of continuum states, we determine the parameters, α_n and β_n, such that the sum

$$S_n(\alpha_n,\beta_n) = \sum_j \rho_{jn}^2 \quad \text{(V-8)}$$

is minimised. Most of the ratios, ρ_{jn}, are very sensitive to changes in f_n: the residua of the first two or three partial wave couplings are only changed slightly by varying f_n; but those for all higher partial waves vary by <u>orders of magnitude</u>, and the <u>same</u> choice of f_n reduces all of them together. The ρ_{jn} are typically much more sensitive to β than to α.

The sum in equation (V-8) may include all of the partial waves considered (up to L' = 10 or 12), or it may include only some of them--as long as the higher ones are included. In searching for the minimum, I found it convenient to omit the first two or three partial wave couplings, because of their insensitivity to changes in f_n; the minimum is much more sharply defined when they are excluded. However, the "optimum" values obtained for $\beta_n(R)$ (to three significant figures), and $\alpha_n(R)$ (to two sig. figs.) remain unchanged.

This process is repeated for other, arbitrarily chosen, energies, and for all possible types of coupling from the state, $|n\rangle$, at a series of R-values; and the values of the "optimum" parameters are compared. The results are described in the next section.

C. Results of Calculations

1. Behaviour of Optimum Parameters

(a) The precision with which the optimum parameters can be determined depends on three factors: (1) the sharpness of the minima in S_n^L, (2) the agreement between determinations using different continuum energies, and (3) the agreement using different types of coupling. Usually, these factors are commensurable, and we can determine β_n to three significant figures and α_n to two significant figures.

(b) In every case, the optimum parameters are independent of continuum energy.

(c) In all cases (except for the 3dσ state; see items (e) and (h), below), the optimum parameters are the same for radial couplings from |n> as for angular couplings; in particular, this is true for the 2pπ state, which is linked by angular couplings to both σ and δ continuum states.

(d) I have redetermined the parameters, $\beta_n(R)$, for both radial and angular couplings from the $1s\sigma_g$, $2p\sigma_u$, and $2p\pi_u$ states of H_2^+, which were reported in reference 2. The new values lie well within the (graphically estimated) ranges given in reference 2a, for the radial parameters, but do not always agree with the estimated angular parameters of reference 2b. The present numbers are the more reliable.

(e) I have also determined $\beta_n(R)$ for the $2s\sigma_g$ and $3d\sigma_g$ states of H_2^+. However, for the $3d\sigma_g$ state, the angular couplings are not very sensitive to the choice of β, and the resulting minimum is nearly flat for $0.02 \leq \beta \leq 0.10$. I have taken $\beta_n^{\Theta} = \beta_n^{R}$ here, as is found for every other case.

(f) I have studied the 1sσ, 2sσ, 2pσ, 2pπ, and 3dσ states of the asymmetric HeH^{++} system, and the 1sσ, 2pσ, and 2pπ states of the intermediate model systems with Z_B = 1.0, and Z_A = 1.2, 1.4, 1.6, and 1.8. If f_n is described by equation (V-7), the effects of charge asymmetry are very well accounted for, and we can take the optimum values of $\beta_n(R)$ to be the <u>same</u> as those for H_2^+. Typically, the S_n surface has a deep, somewhat elongated depression in the (α,β) plane, running almost parallel to the α-axis. Within this entire region, the residua for the higher partial waves are all of the order 10^{-3} to 10^{-4}. Therefore, <u>small</u> changes in $\beta_n(R)$ may be offset by compensating <u>larger</u> changes in $\alpha_n(R)$, while remaining in the optimum region. In most cases (but see item (g), below), the range of acceptable β-values does not vary from the H_2^+ values by more than 1% to 4%. The important point is that no <u>significant</u> further reduction of coupling matrix elements occurs elsewhere in the valley.

The optimum $\alpha_n(R)$ vary slowly with charge asymmetry.

(g) At distances, $R \geq 2$ to 4 au, the optimum parameters for the $1s\sigma$ and $2s\sigma$ states of HeH^{++} cannot be so precisely determined. Even at short distances, these states are dominantly <u>atomic</u> states of the He^+ ion, and the appropriate switching function is -1. There is a wide range of parameters, α and β, yielding that simple result. At larger R-values ($R \geq 12$ au), this becomes the characteristic situation for most of the molecular states of HeH^{++}; in effect, the deep, elongated valley described above becomes very long and very broad. This is to be expected, because the very simple "atomic" switching functions, $f = f_J$, are always asymptotically correct. However, the 1sσ and 2sσ states of HeH^{++} are the only cases where such very simple choices can produce efficient reduction of the spurious pss couplings at the small to moderate distances where the physically real couplings occur.

(h) As in the case of H_2^+, I found that the angular coupling matrix elements for the 3dσ state of HeH^{++} are not very sensitive to changes in α and β, and I have again taken $\alpha^\Theta = \alpha^R$, and $\beta^\Theta = \beta^R$.

Figure 8 shows the values of $\beta_n(R)$ vs. R, determined for H_2^+. For the 3dσ_g state, the crosses represent the values determined for the radial couplings alone. For the remaining states, where an error bar appears, it indicates the difference between "best" values for $\beta_n(R)$ obtained from radial and from angular couplings; where only a cross appears, this difference is too small to be shown. Figure 9 depicts $\alpha_n(R)$ vs. R, for HeH^{++} (β_n values are those for H_2^+). Error bars and crosses have the same meaning as in figure 8. The large uncertainties in $\alpha_{1s\sigma}$ and $\alpha_{2s\sigma}$ are related to the simple behaviour of the switching functions for these states.

Figures 10 and 11 are plots of the "optimum" switching functions for H_2^+ and HeH^{++} vs. η, at R = 8.0 au. In figure 12, I have shown the behaviour of the switching function for the 1sσ state, as a function of Z_A, again at

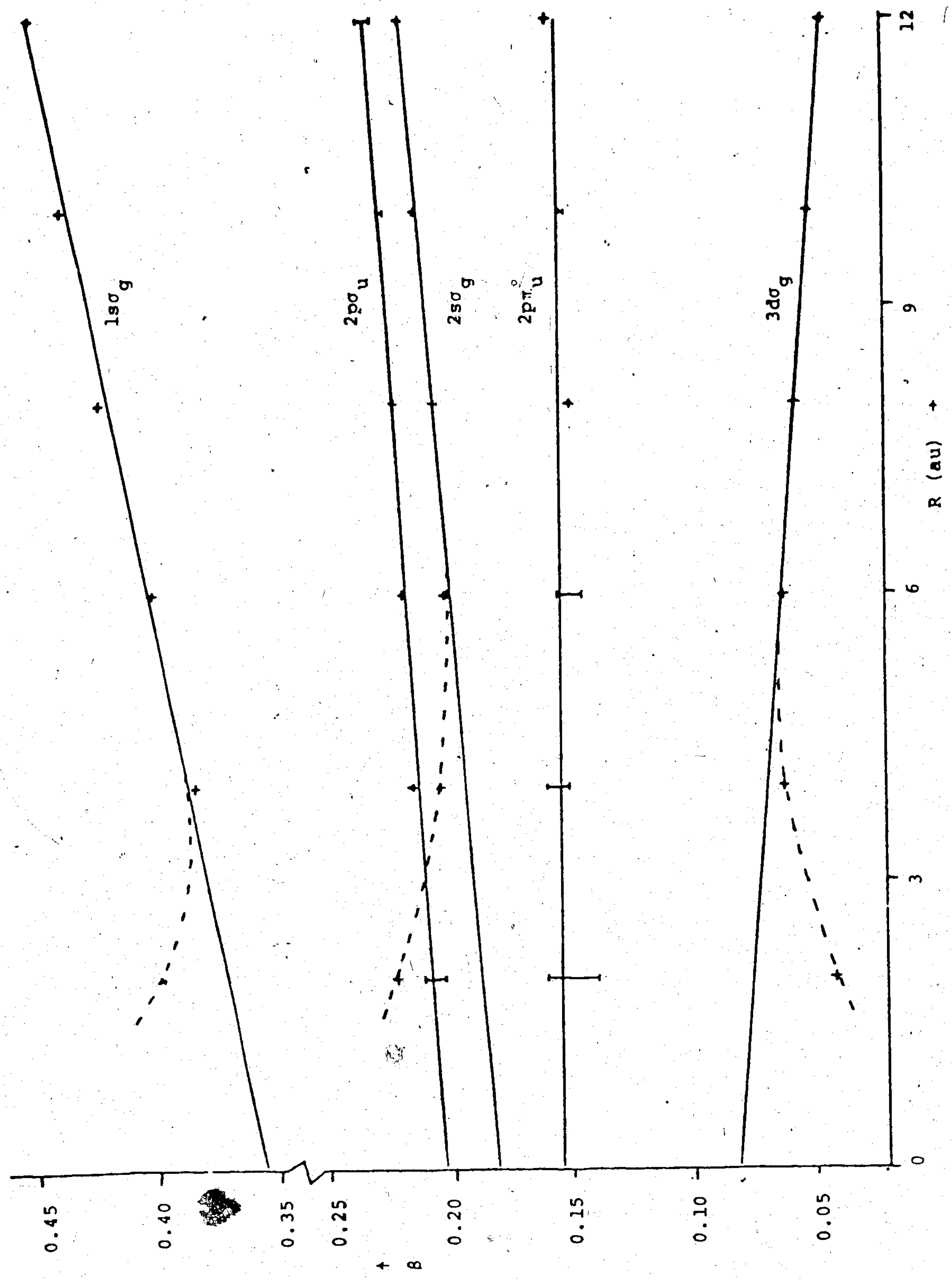

Figure 8. "Optimum" β_n's, for H_2^+

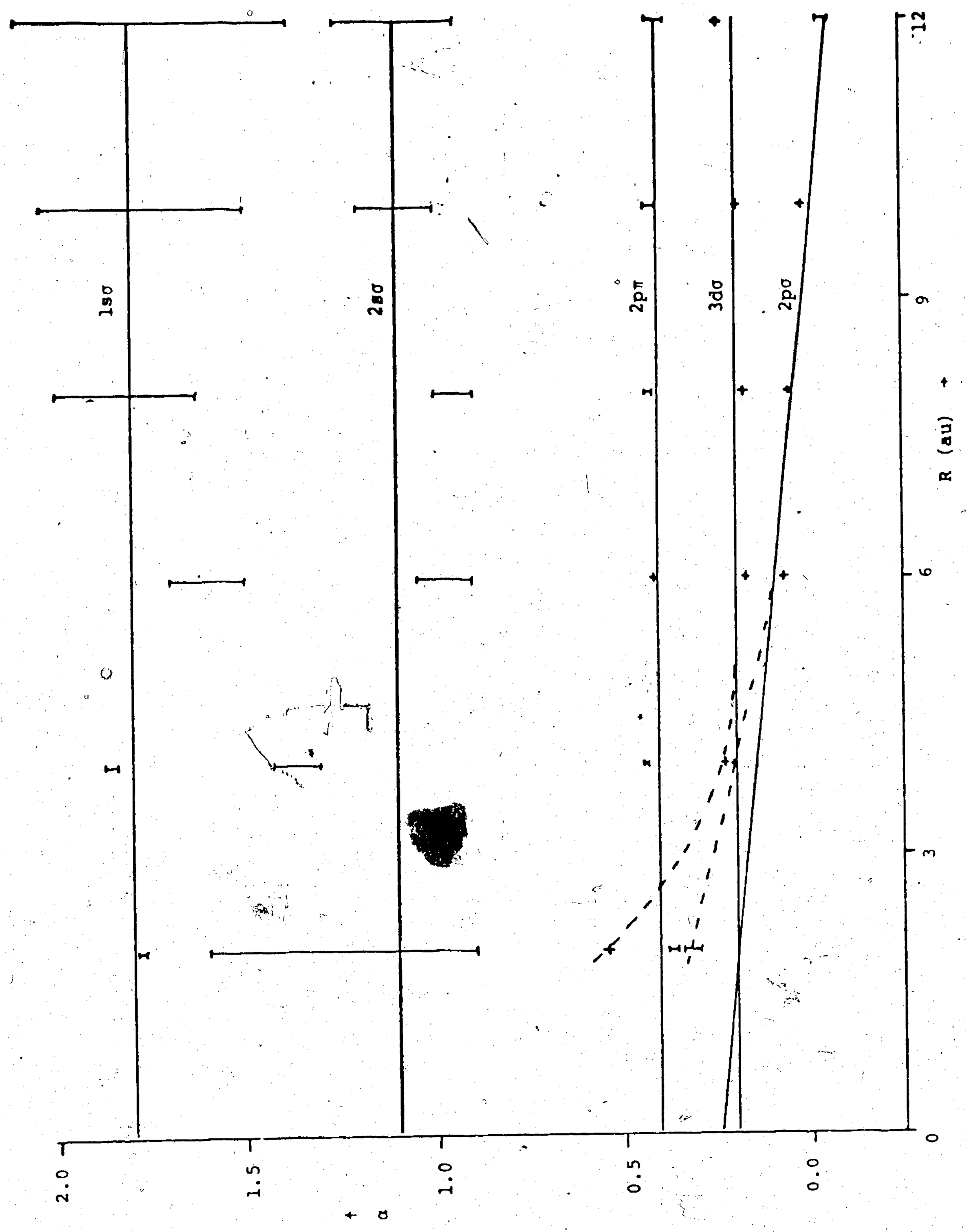

Figure 9. "Optimum" α_n's, for HeH^{++}

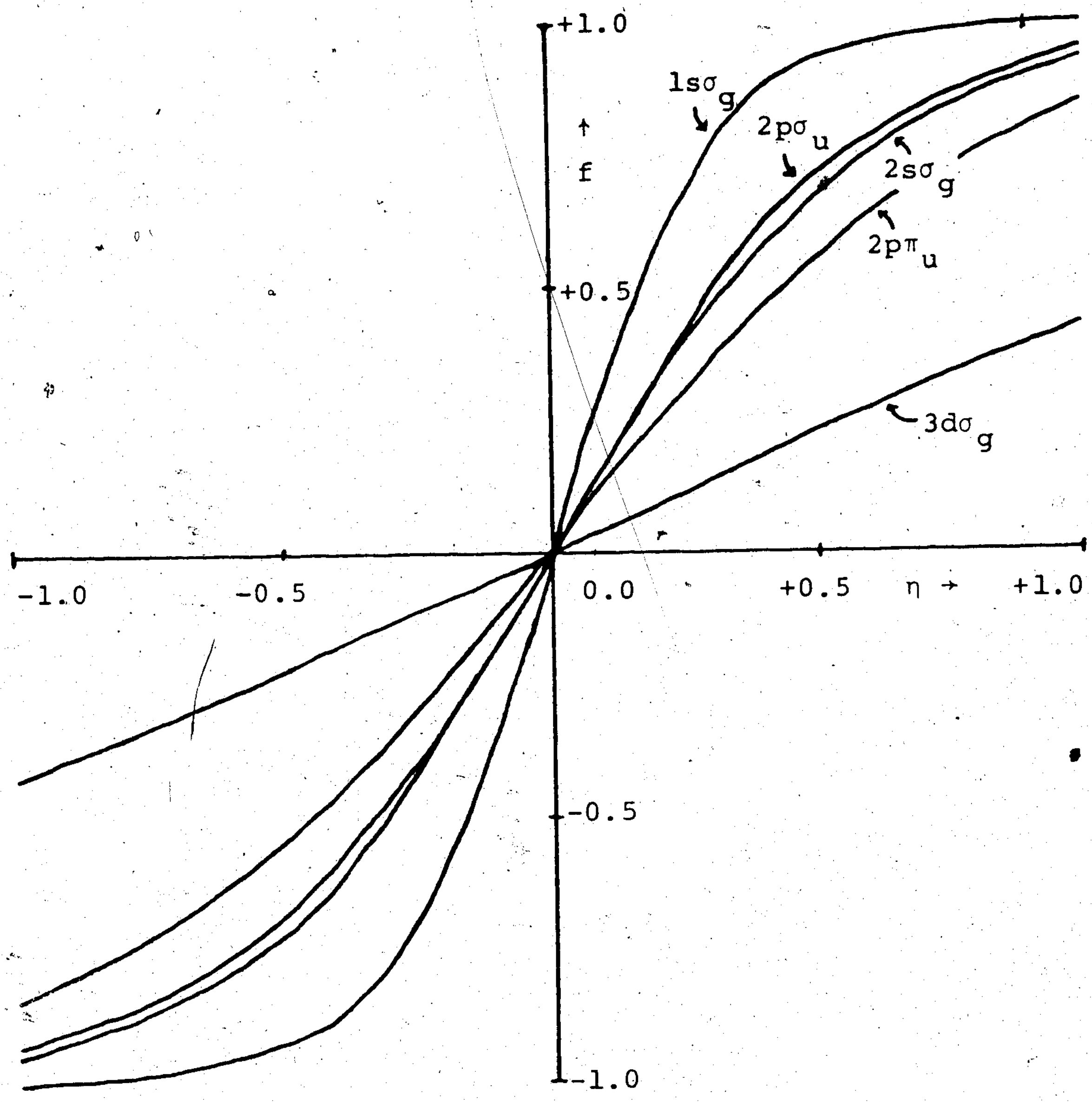

Figure 10. "Optimum" f_n's, for H_2^+, at R = 8.0 au

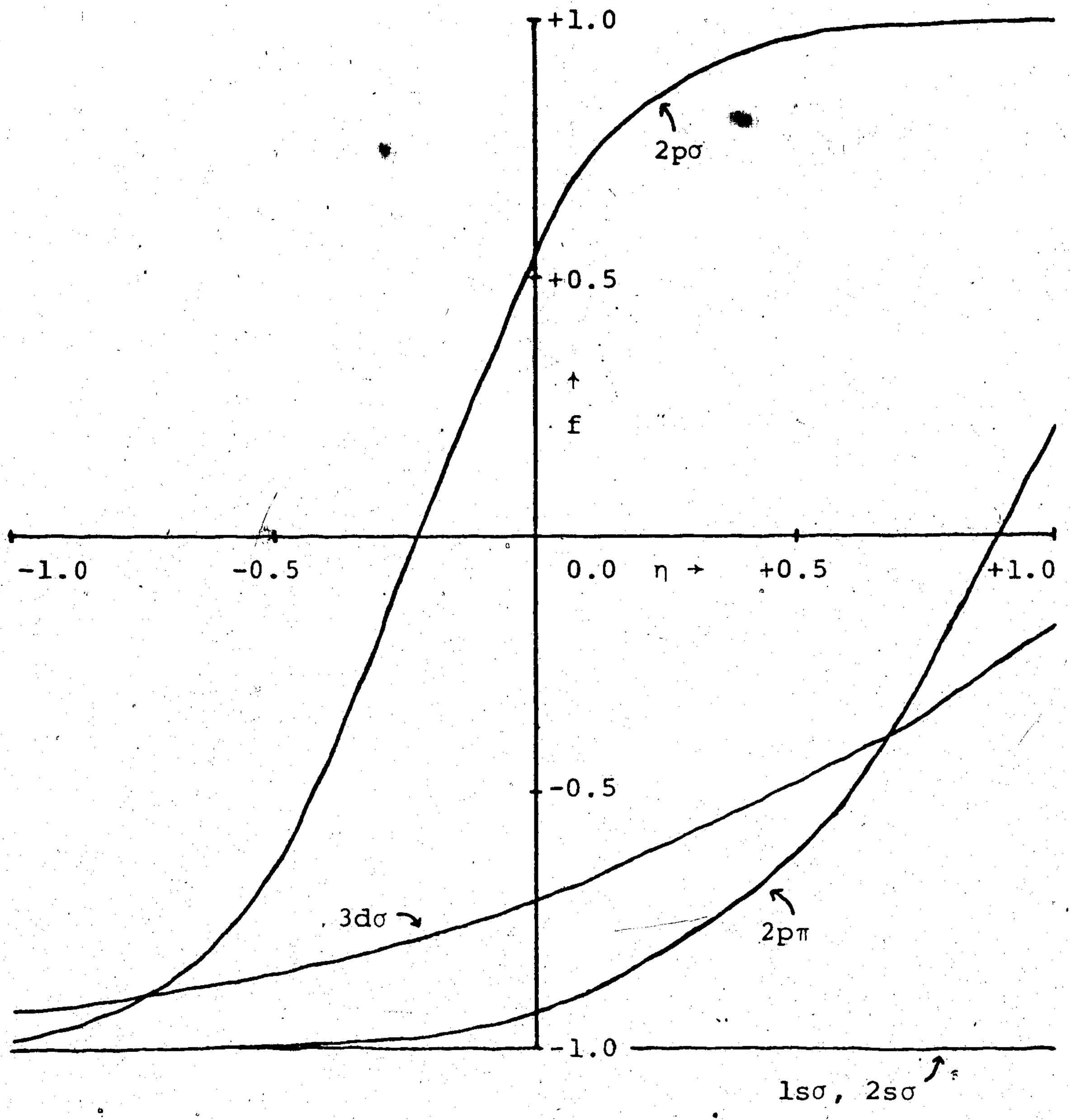

Figure 11. "Optimum" f_n's, for HeH^{++}, at R = 8.0 au

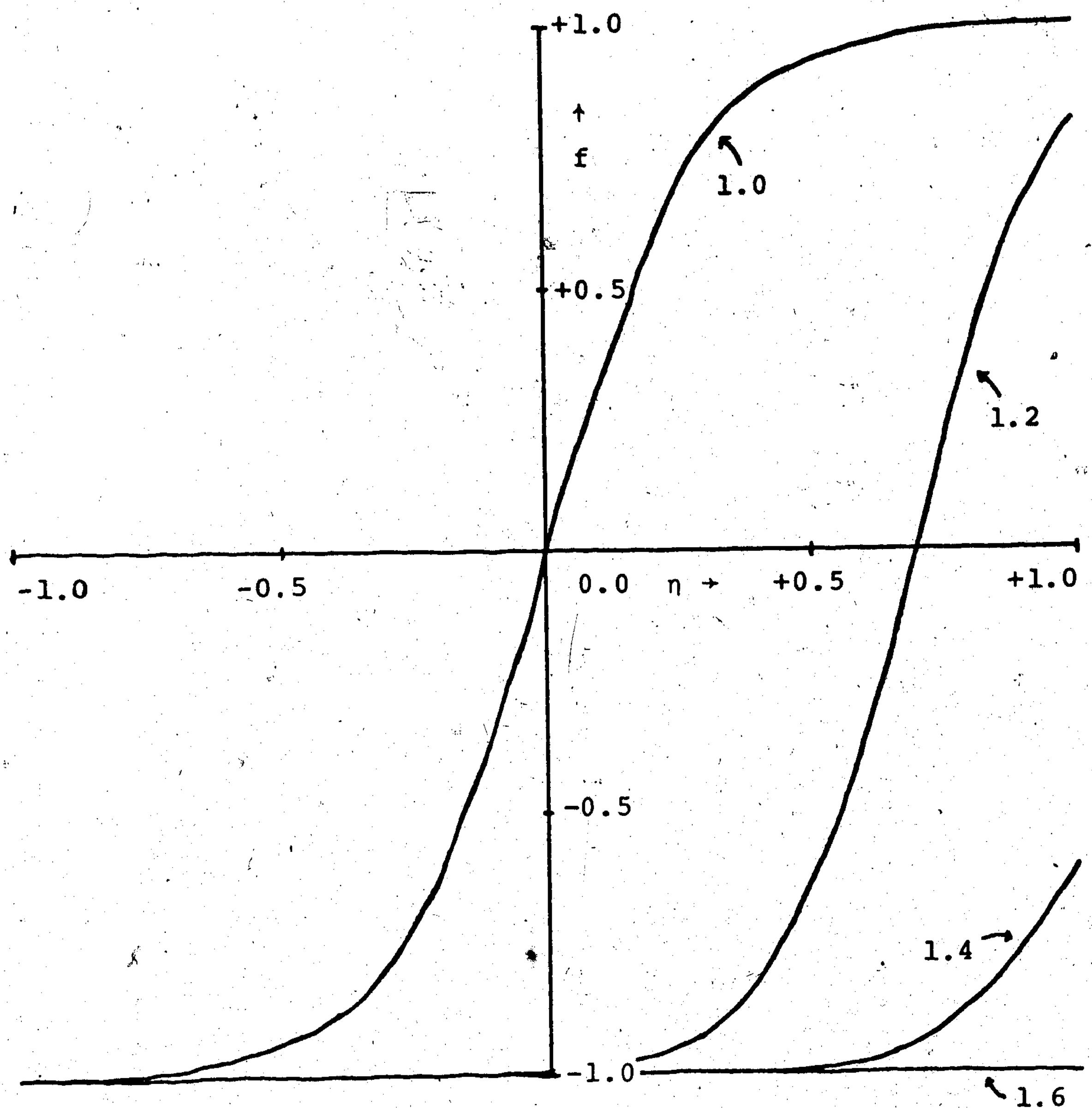

Figure 12. "Optimum" $f_{1s\sigma}$'s, as a function of Z_A, with Z_B = 1.0, and R = 8.0 au

$R = 8.0$ au. This illustrates very clearly the development of the atomic character of $f_{1s\sigma}$, as Z_A increases.

Table 5 gives detailed results for the "optimum" parameter, β_n. Tables 6 to 9 show the "optimum" values of α_n, as a function of Z_A.

2. Matrix Elements

To compute corrected nonadiabatic couplings to the continuum, I have used the straight-line approximations for both $\beta_n(R)$ and $\alpha_n(R)$ vs. R, which are shown in figures 8 and 9. It would appear from the figures that this might introduce large errors in the matrix elements at small values of R, but this is not the case. For $R \leq 4$ au, the matrix elements to higher partial waves are extremely small, while the couplings to the lower partial waves are not very sensitive to changes in the switching function parameters. Whether such departures from the "optimum" parameters can be used in computing discrete to discrete couplings is not so clear.

I have calculated the corrected matrix elements for the five discrete states mentioned, for H_2^+ and HeH^{++}. The corrected matrix elements for all but the first few partial waves are negligible, and these few are usually significantly reduced in size and range. By contrast, the pss couplings are all large and very long ranged.

Notation in the figures labels bound states ($|nLm\rangle$), and continuum states ($\langle\varepsilon'L'm'|$), where n is the united

TABLE 5

"OPTIMUM" β_n's, DETERMINED FOR H_2^+

	1sσ		2sσ		2pσ	
R	$\hat{L}_y$	$\partial/\partial R$	$\hat{L}_y$	$\partial/\partial R$	$\hat{L}_y$	$\partial/\partial R$
2	.399	.400	.2231	.2239	.212	.203
4	.385	.385	.2050	.2053	.216	.217
6	.402	.403	.2033	.2037	.220	.220
8	.424	.424	.2073	.2073	.224	.223
10	.439	.439	.2136	.2135	.229	.227
12	.450	.451	.2200	.2201	.237	.231

	2pπ			3dσ
R	$\hat{L}_-$	$\hat{L}_+$	$\partial/\partial R$	$\partial/\partial R$
2	-	-	.161	.042
4	.161	.160	.152	.063
6	.157	.155	.146	.063
8	.149	.151	.151	.058
10	.152	.154	.154	.052
12	.159	.159	.159	.046

TABLE 6

"OPTIMUM" α_n's, FOR THE $1s\sigma$ STATE

	Z_A = 1.2		1.4		1.6		1.8		2.0	
R	$\hat{L}_y$	$\partial/\partial R$	$\hat{L}_y$	$\partial/\partial R$	$\hat{L}_y$	$\partial/\partial R$	$\hat{L}_y$	$\partial/\partial R$	$\hat{L}_y$	$\partial/\partial R$
2	0.68	0.69	1.00	1.01	1.46	1.48	1.99	2.03	1.77	1.79
4	1.29	1.29	1.23	1.22	1.59	1.64	2.14	2.14	1.87	1.84
6	1.71	1.73	1.75	1.82	2.04	1.98	1.7	1.5	1.7	2.0
8	2.09	2.13	2.39	2.29	2.3	2.0	2.3	2.0	2	2
10	2.24	2.29	3.0	2.8	2.5	2.8	3	3	-	-
12	2.62	2.90	3.5	3.5	3	3	-	-	-	-

TABLE 7

"OPTIMUM" α_n's, FOR THE 2pσ STATE

	$Z_A = 1.2$		1.4		1.6		1.8		2.0	
R	$\hat{L}_y$	$\partial/\partial R$	$\hat{L}_y$	$\partial/\partial R$	$\hat{L}_y$	$\partial/\partial R$	$\hat{L}_y$	$\partial/\partial R$	$\hat{L}_y$	$\partial/\partial R$
2	+.35	+.37	+.36	+.39	+.29	+.33	+.30	+.33	+.30	+.34
4	+.01	+.01	+.09	+.09	+.13	+.14	+.18	+.18	+.21	+.21
6	-.32	-.33	-.12	-.13	-.03	-.04	+.03	+.02	+.07	+.07
8	-.45	-.46	-.32	-.34	-.07	-.08	+.00	-.01	+.06	+.05
10	-.69	-.70	-.55	-.59	-.20	-.21	-.11	-.05	+.02	+.02
12	-1.0	-1.2	-.89	-.99	-.22	-.23	-.14	-.14	-.02	-.06

TABLE 8

"OPTIMUM" α_n's, FOR THE $2p\pi$ STATE

	Z_A = 1.2		1.4		1.6		1.8		2.0	
R	$\hat{L}_+$ $\hat{L}_-$	$\partial/\partial R$	$\hat{L}_+$ $\hat{L}_-$	$\partial/\partial R$	$\hat{L}_+$ $\hat{L}_-$	$\partial/\partial R$	$\hat{L}_+$ $\hat{L}_-$	$\partial/\partial R$	$\hat{L}_+$ $\hat{L}_-$	$\partial/\partial R$
2	-	-	-	-	0.40	0.40	0.39	0.40	0.38	0.37
	-		-		0.40		0.41		0.37	
4	0.31	0.37	0.43	0.37	0.40	0.40	0.43	0.42	0.45	0.44
	0.31		0.42		0.41		0.44		0.44	
6	0.43	0.43	0.39	0.39	0.41	0.41	0.42	0.42	0.42	0.42
	0.42		0.40		0.40		0.43		0.44	
8	0.43	0.42	0.42	0.42	0.42	0.42	0.43	0.41	0.44	0.42
	0.43		0.43		0.42		0.43		0.44	
10	0.48	0.48	0.46	0.45	0.44	0.43	0.45	0.41	0.44	0.41
	0.48		0.46		0.43		0.42		0.41	
12	0.55	0.53	0.49	0.45	0.46	0.42	0.44	0.41	0.43	0.38
	0.55		0.49		0.45		0.42		0.39	

TABLE 9

"OPTIMUM" α_n's, FOR HeH^{++}

(a) 2sσ state

	R = 2	4	6	8	10	12
$\hat{L}_y$	0.88	1.43	1.05	0.95	1.2	1.2
$\partial/\partial R$	1.6	1.28	0.91	0.92	1.0	0.9

(b) 3dσ state

	R = 2	4	6	8	10	12
$\partial/\partial R$	0.55	0.23	0.17	0.17	0.19	0.24

atom principal quantum number, ε' is the continuum electronic energy (in Rydbergs); L, L' are united atom orbital angular momentum quantum numbers; and m, m' are azimuthal quantum numbers; distance, R, is in au. The matrix elements shown are related to those defined in equations (IV-5) and (IV-9) as follows:

$$\langle \varepsilon' L' m | H(RAD) | nLm \rangle = (i/\hbar)\ [P^g + A^g]^R_{jn}, \qquad (V\text{-}9a)$$

$$\langle \varepsilon' L' m \pm 1 | H(ANG) | nLm \rangle = (i/2\mu\hbar)\ [P^g + A^g]^\Theta_{jn}. \qquad (V\text{-}9b)$$

For convenience, I have taken $\mu = 1836.1\ m_0$ (proton rest mass). Table 10 provides a guide to the figures.

Figure 13 shows the disastrous long-range behaviour of the uncorrected pss matrix elements, here shown for H_2^+; the corresponding corrected matrix elements (dashed curves) are negligible. Of course, at the large distances shown, any simple switching function which has the value +1, in the entire neighbourhood of nucleus B, and -1, near A, will produce similar results; the main point of this picture is to illustrate the uncorrected pss couplings.

Figures 14 to 24 compare the uncorrected pss couplings (solid curves) and the corrected couplings (dashed curves), for the various initial states of H_2^+; figures 25 to 35 show the same thing for HeH^{++}. For HeH^{++}, I have also included for comparison the corrected matrix elements

TABLE 10

A GUIDE TO THE FIGURES

		1sσ	2sσ	2pσ	2pπ	3dσ
radial	H_2^+	14	15	16	17	18
	HeH^{++}	25	26	27	28	29
angular	H_2^+	19	20	21	22(L_-) 23(L_+)	24
	HeH^{++}	30	31	32	33(L_-) 34(L_+)	35

————————	pss value
— — — — — —	corrected value with optimum f_n
— – — – —	corrected value with Bates-McCarroll f_n

In all cases, the continuum energy, ε', is 0.50 Ry.

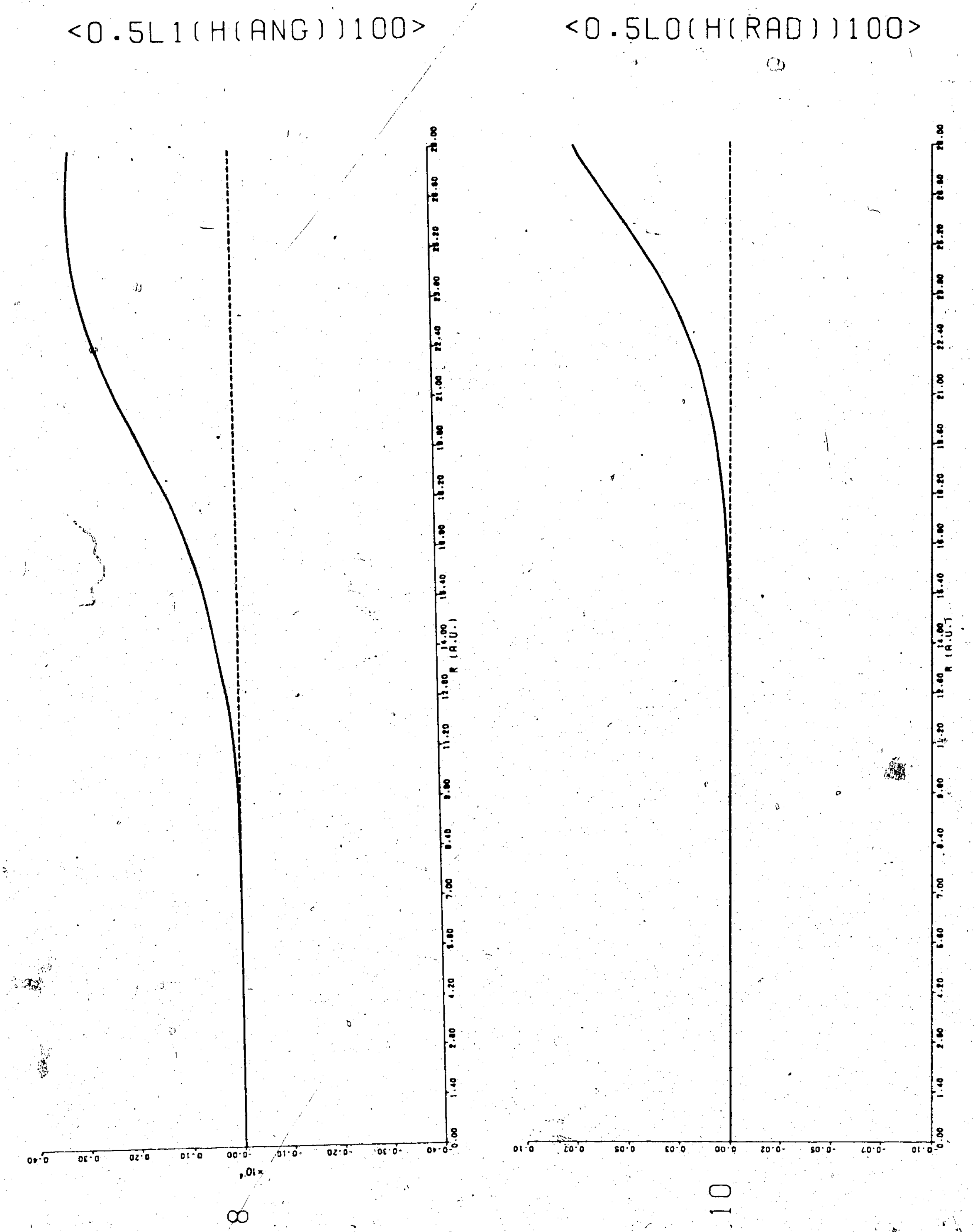

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Figure 13. Long range behaviour of pss matrix elements, shown here for H_2^+

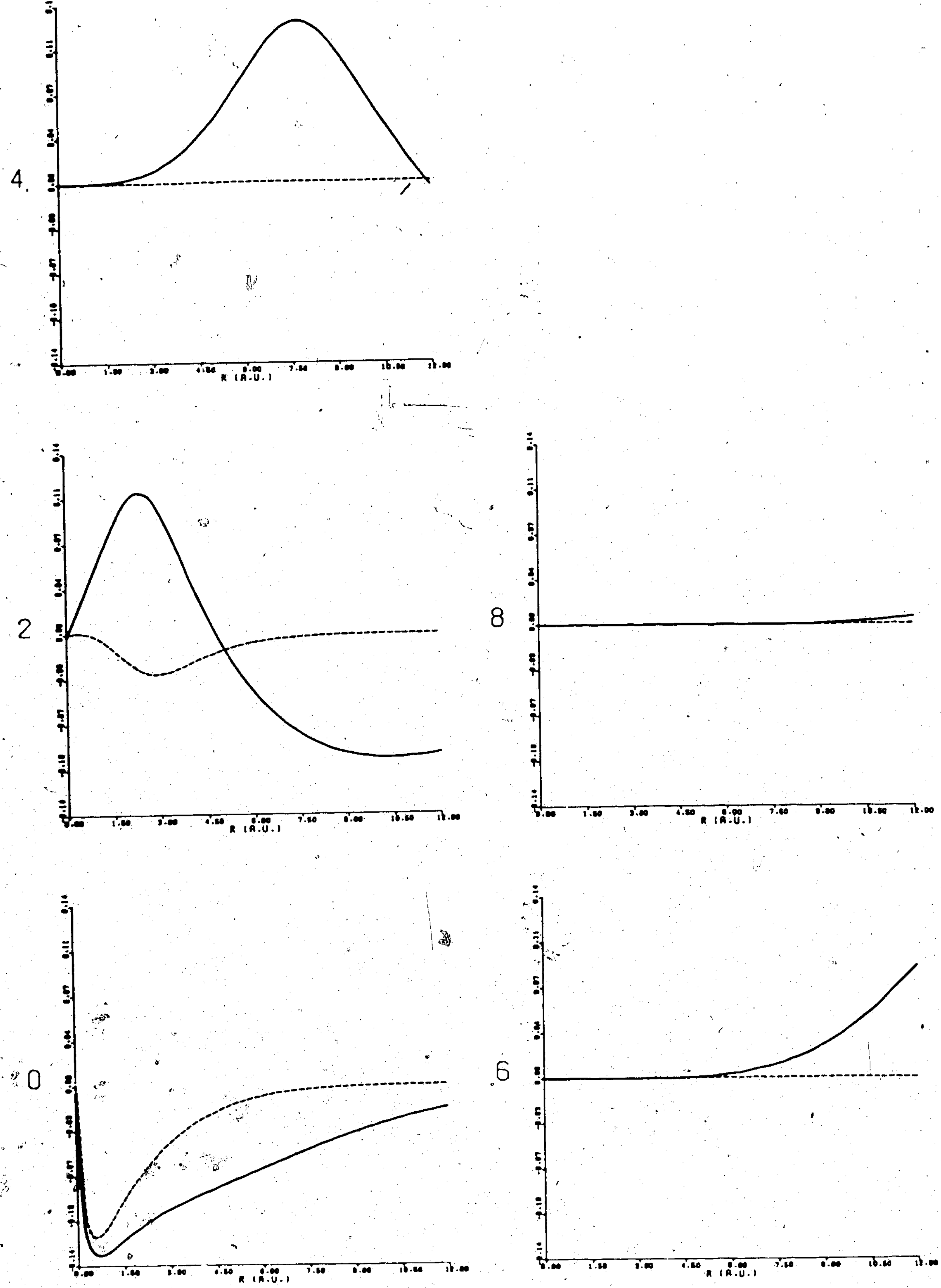

Figure 14. <0.5L'0|H(RAD)|100>, H_2^+, L' = 0(2)8

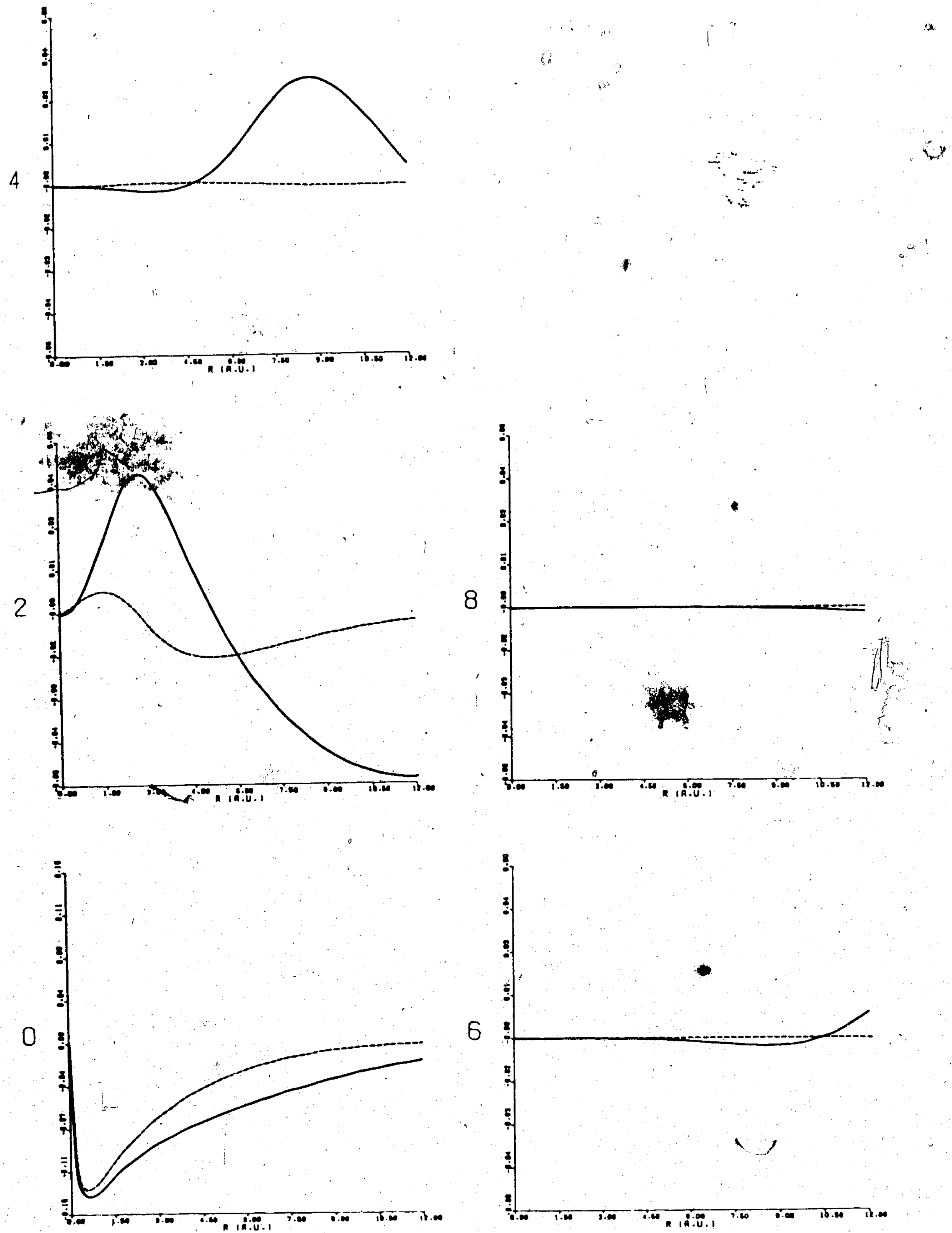

Figure 15. <0.5L'0|H(RAD)|200>, H_2^+, L' = 0(2)8

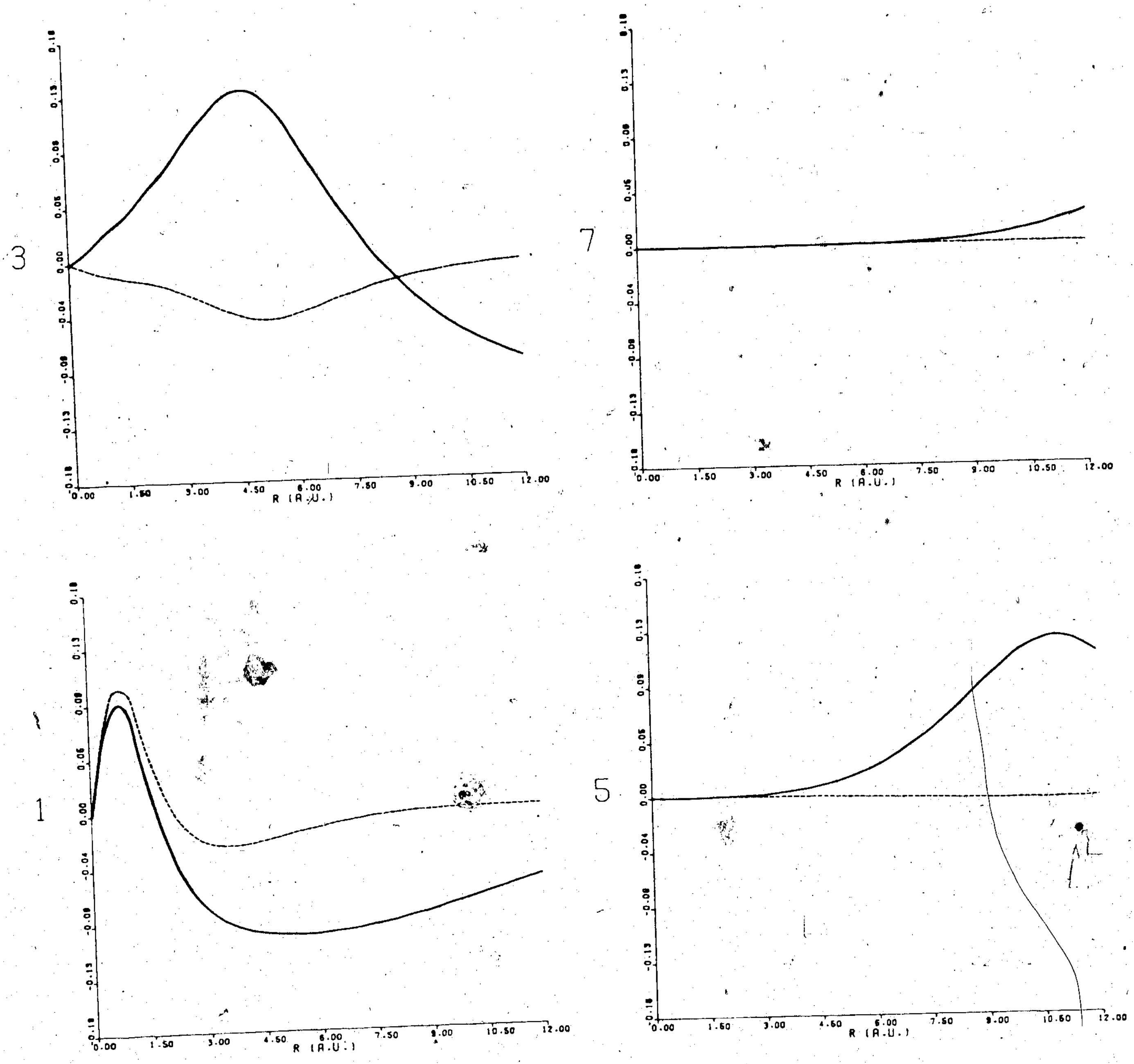

Figure 16. <0.5L'0|H(RAD)|210>, H_2^+, L' = 1(2)7

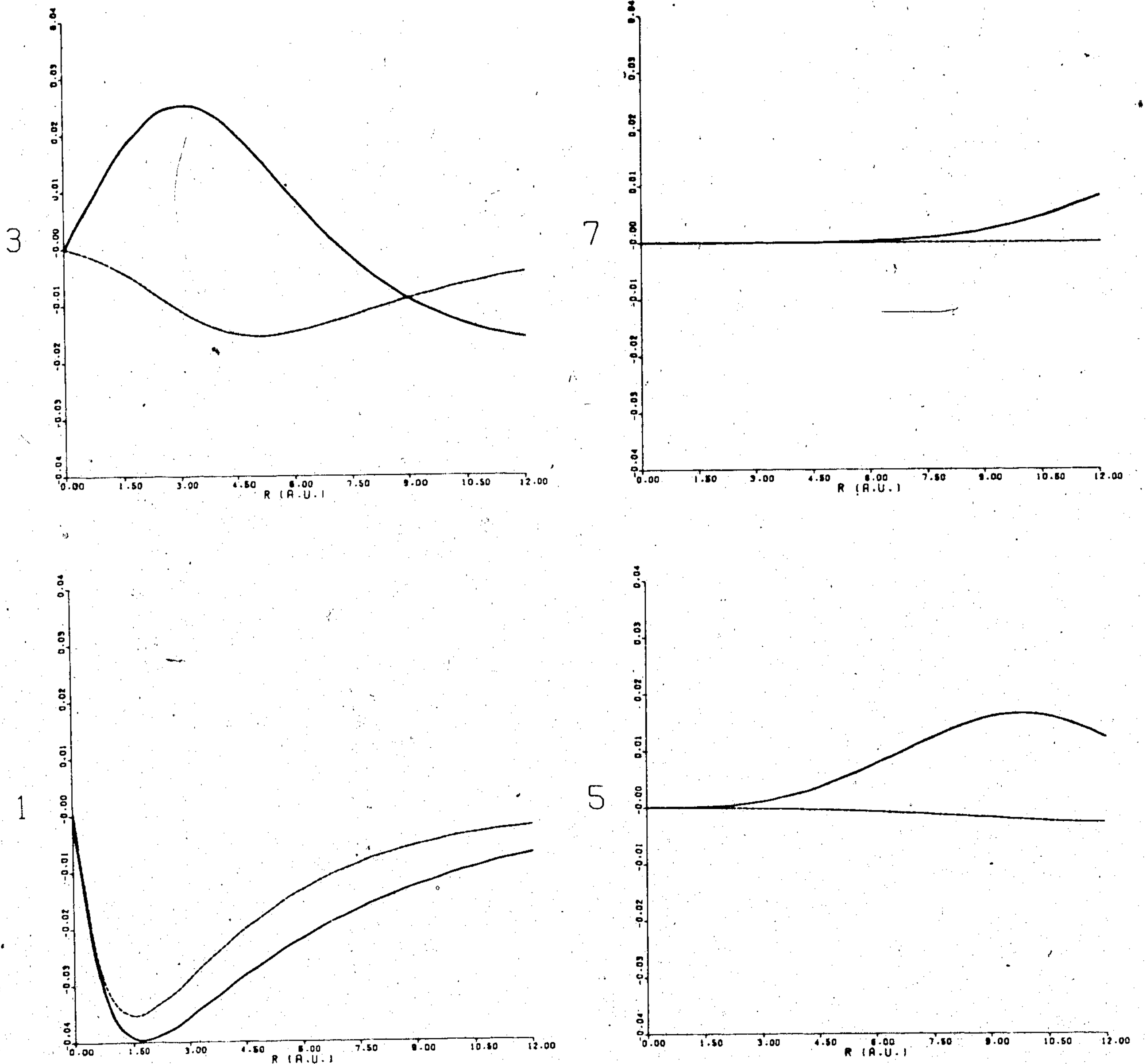

Figure 17. $\langle 0.5L'1|H(RAD)|211\rangle$, H_2^+, L' = 1(2)7

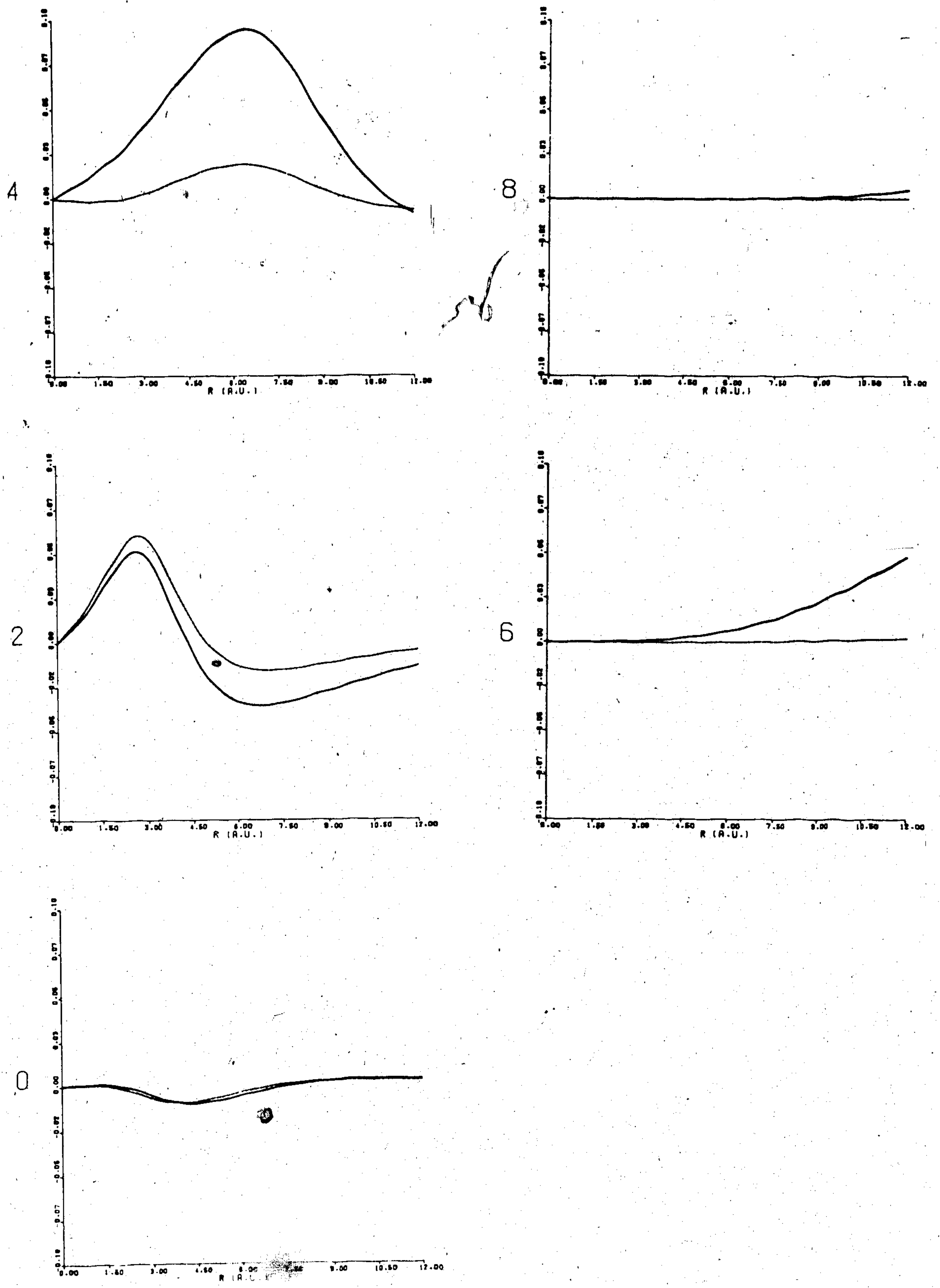

Figure 18. <0.5L'0|H(RAD)|320>, H_2^+, L' = 0(2)8

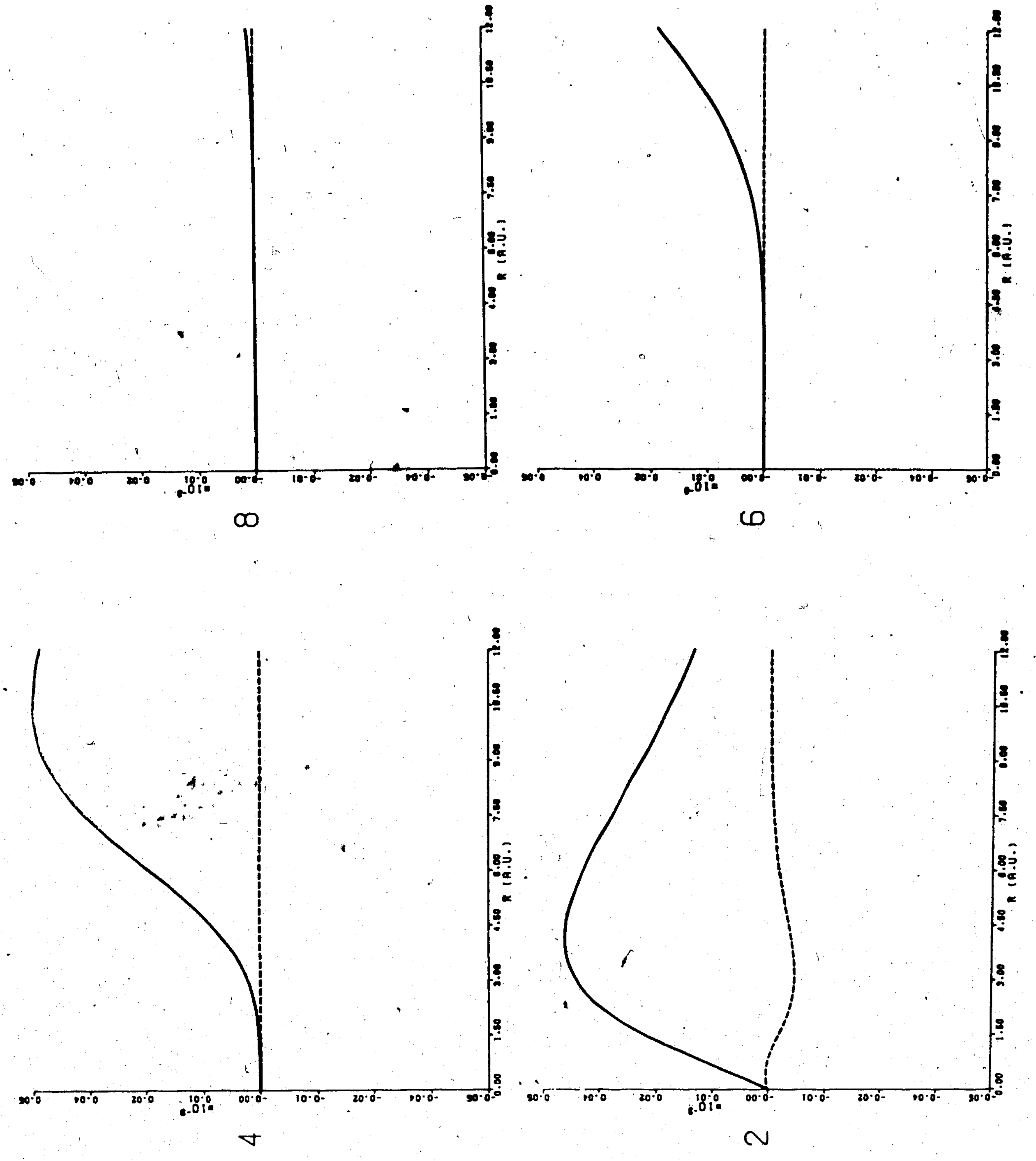

Figure 19. <0.5L'1|H(ANG)|100>, H_2^+, L' = 2(2)8

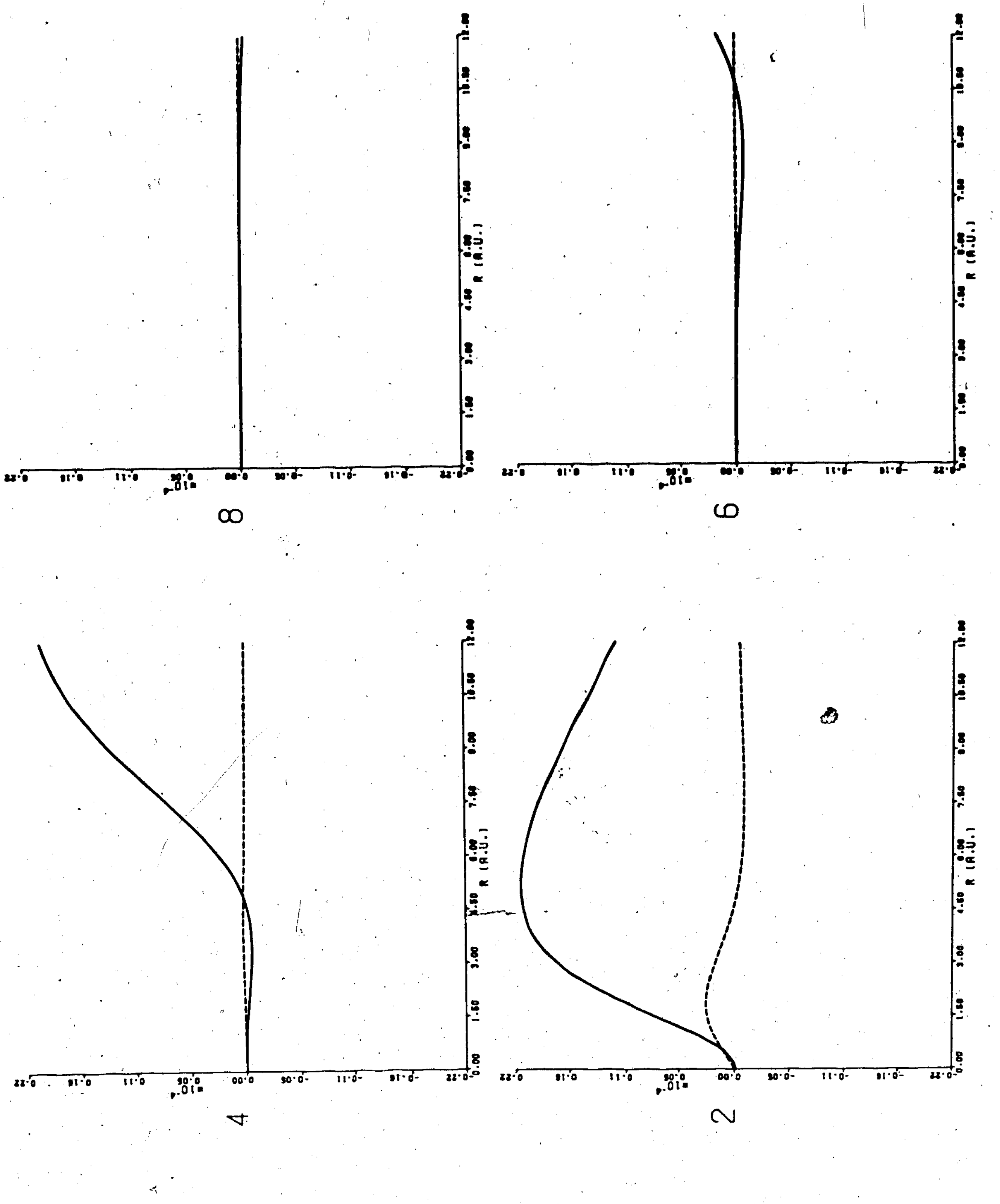

Figure 20. $<0.5L'1|H(ANG)|200>$, H_2^+, L' = 2(2)8

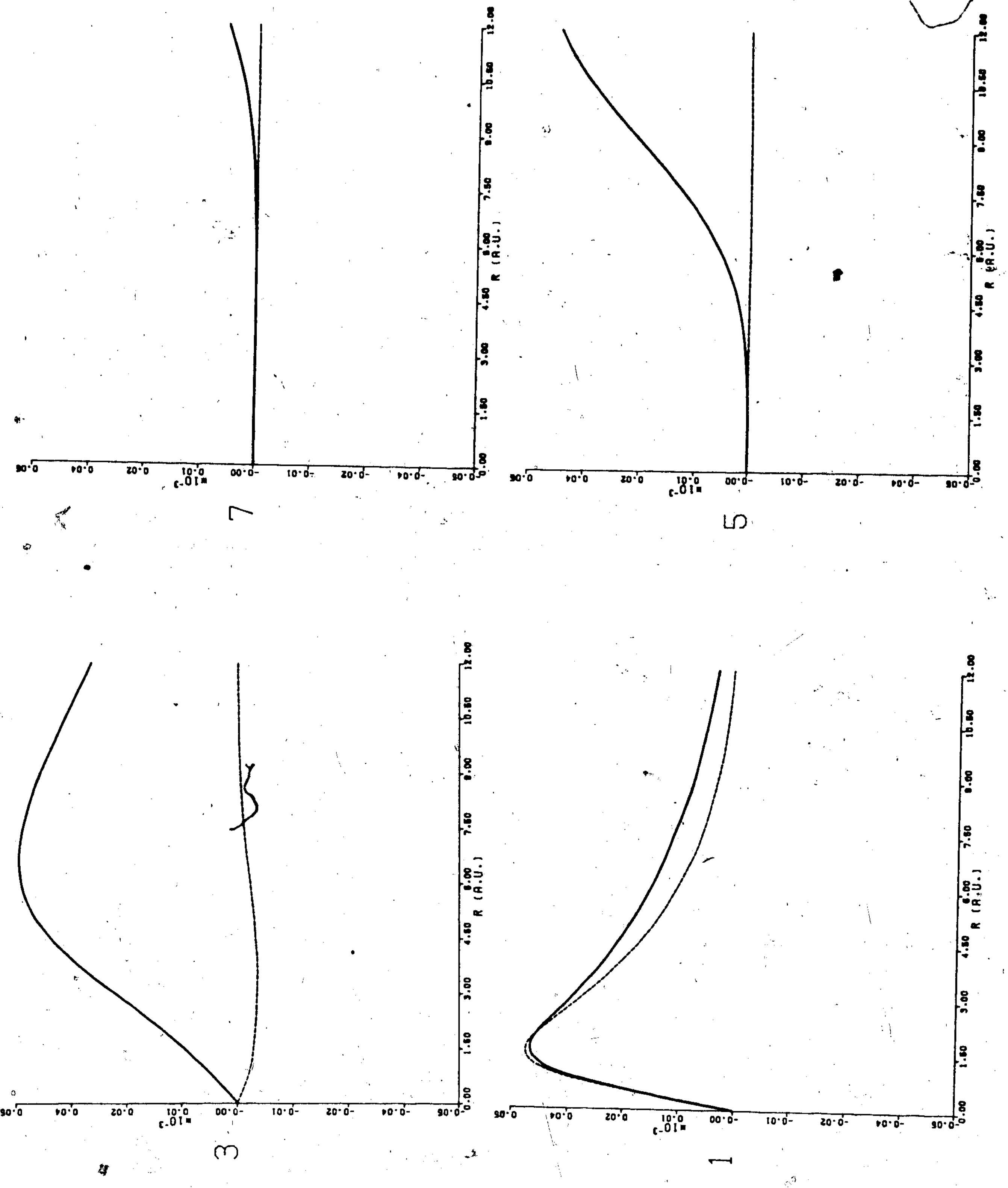

Figure 21. <0.5L'1|H(ANG)|210>, H_2^+, L' = 1(2)7

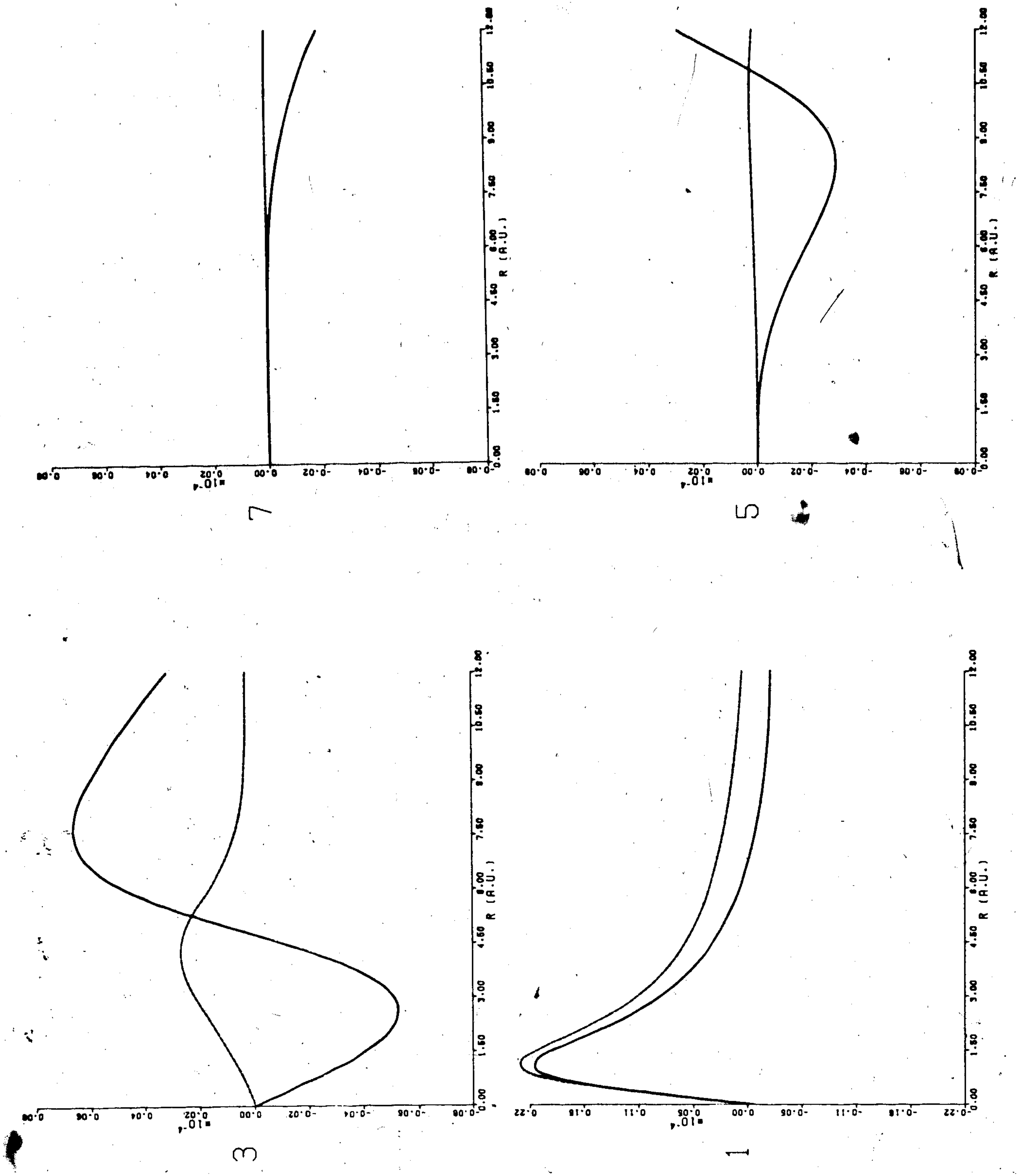

Figure 22. <0.5L'0|H(ANG)|211>, H_2^+, L' = 1(2)7

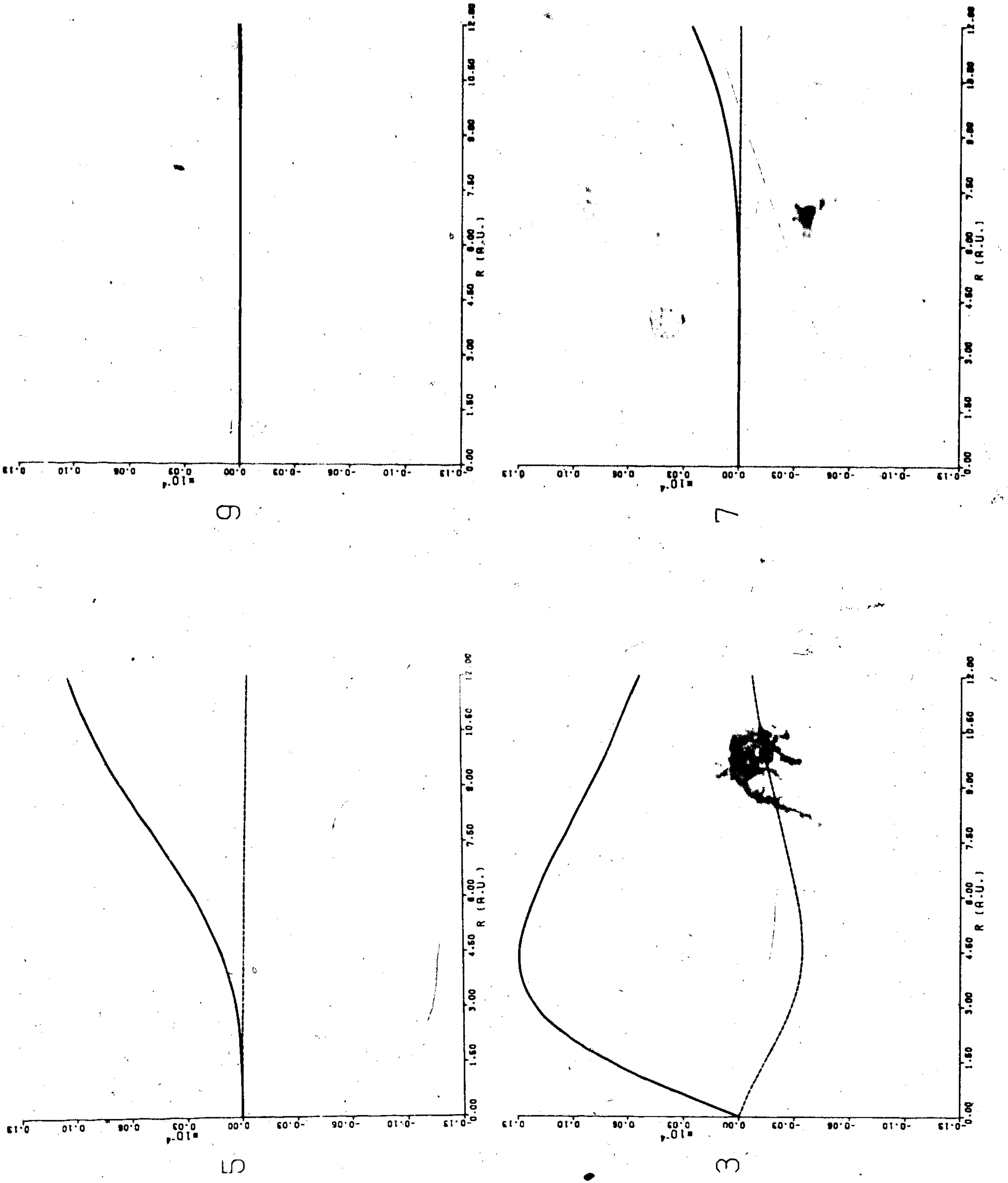

Figure 23. <0.5L'2|H(ANG)|211>, H_2^+, L' = 3(2)9

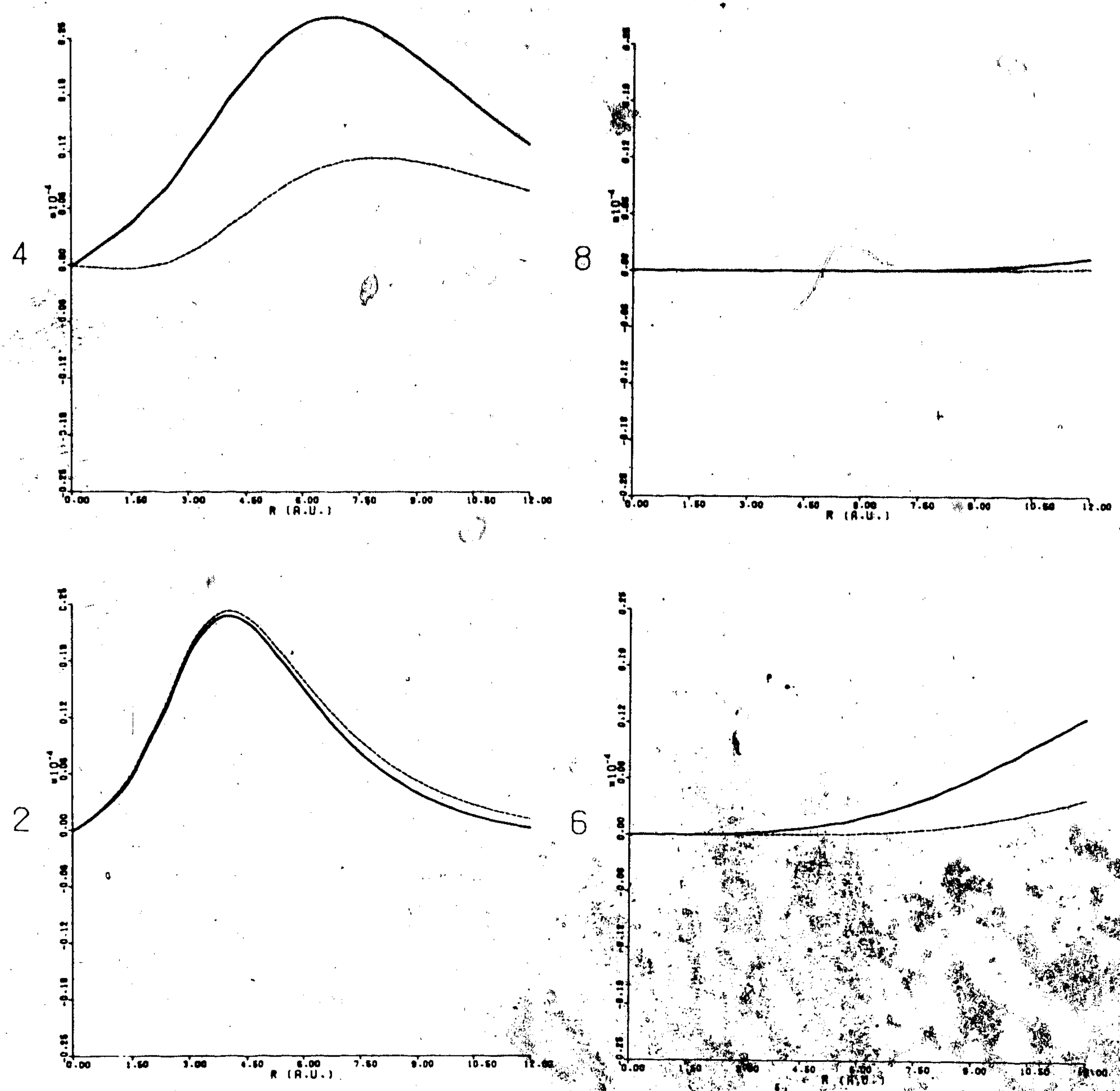

Figure 24. <0.5L'1|H(ANG)|320>, H_2^+, L' = 2(2)8

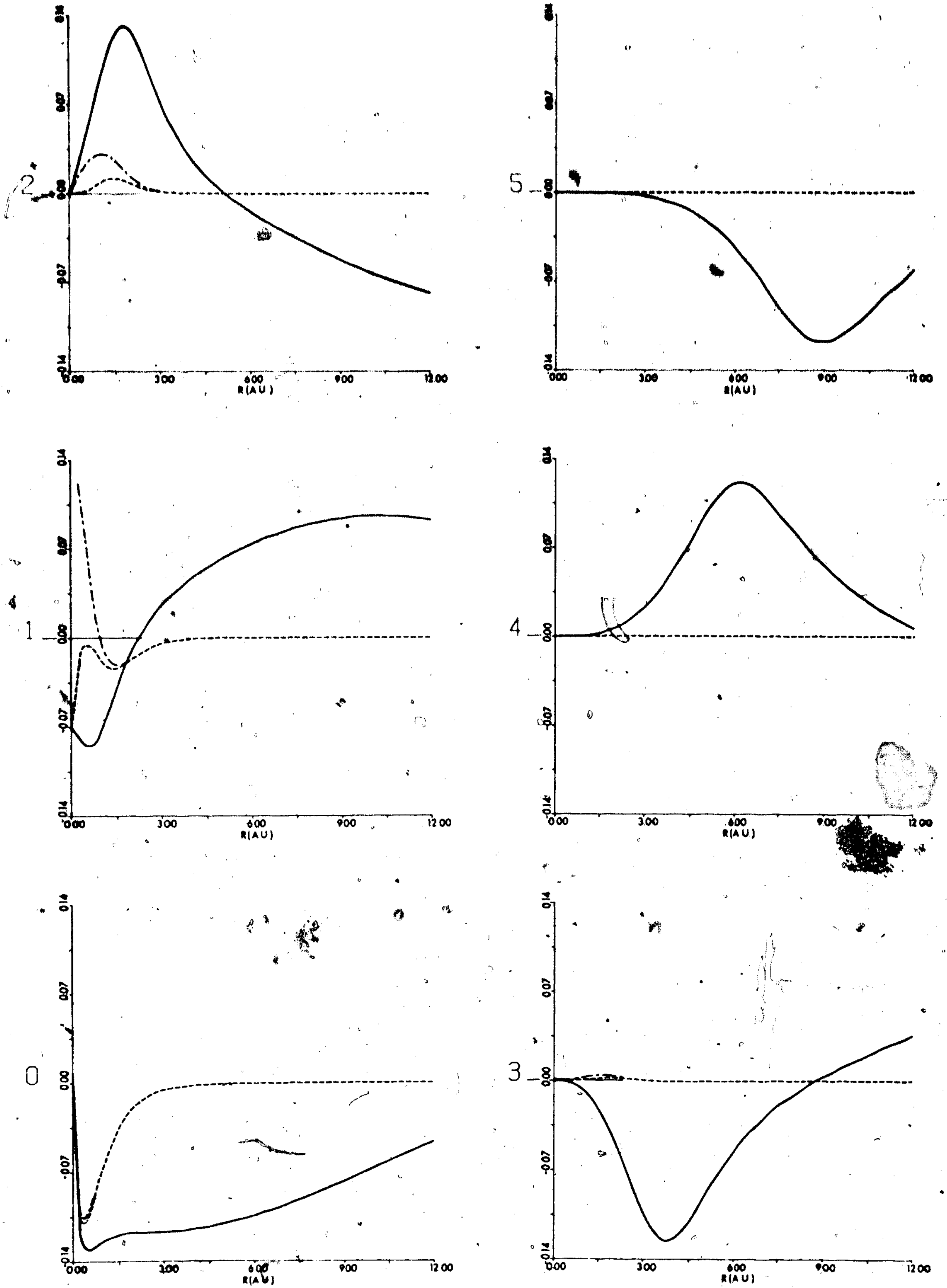

Figure 25. <0.5L'0|H(RAD)|100>, HeH^{++}, L' = 0(1)5

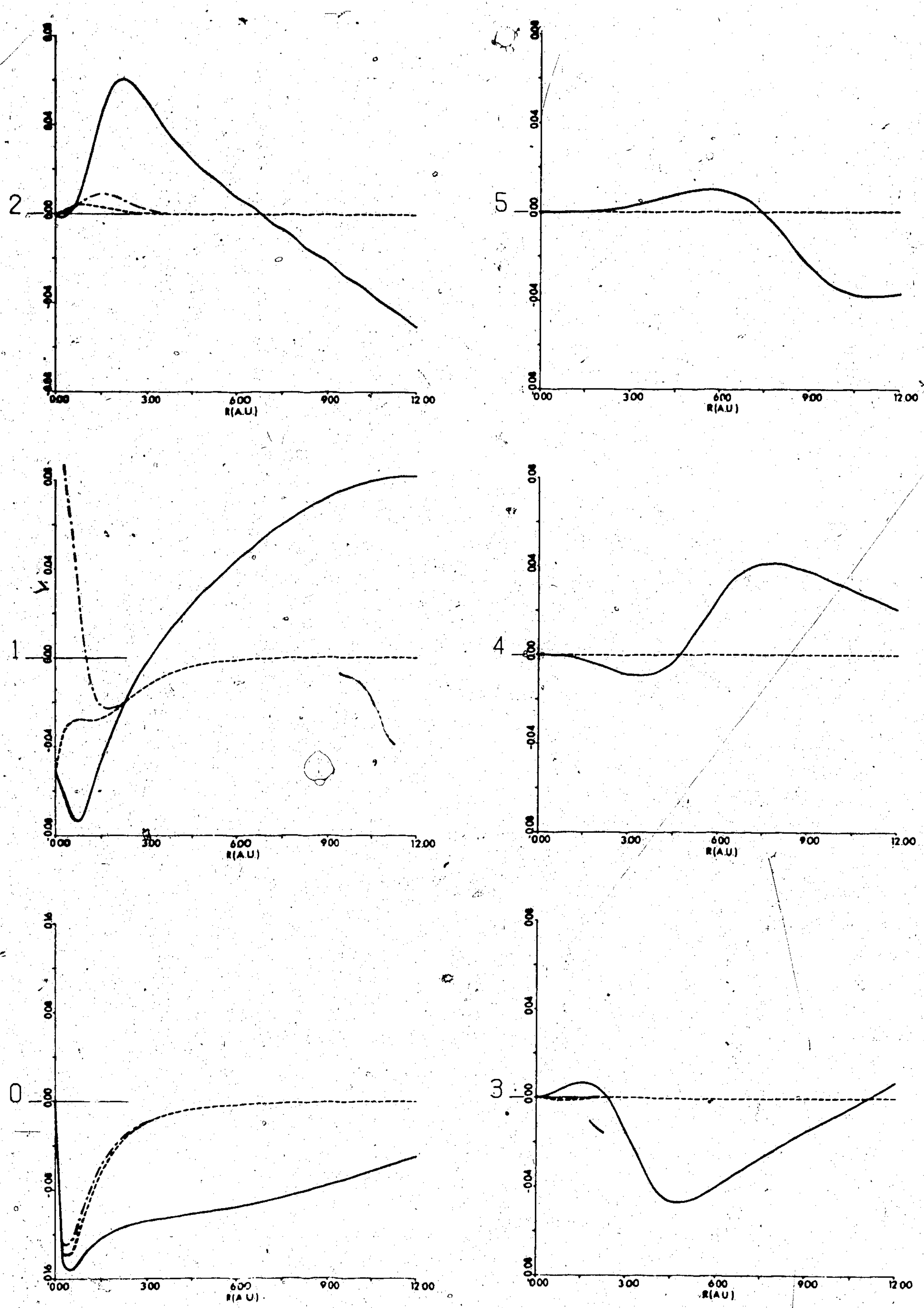

Figure 26. <0.5L'0|H(RAD)|200>, HeH^{++}, L' = 0(1)5

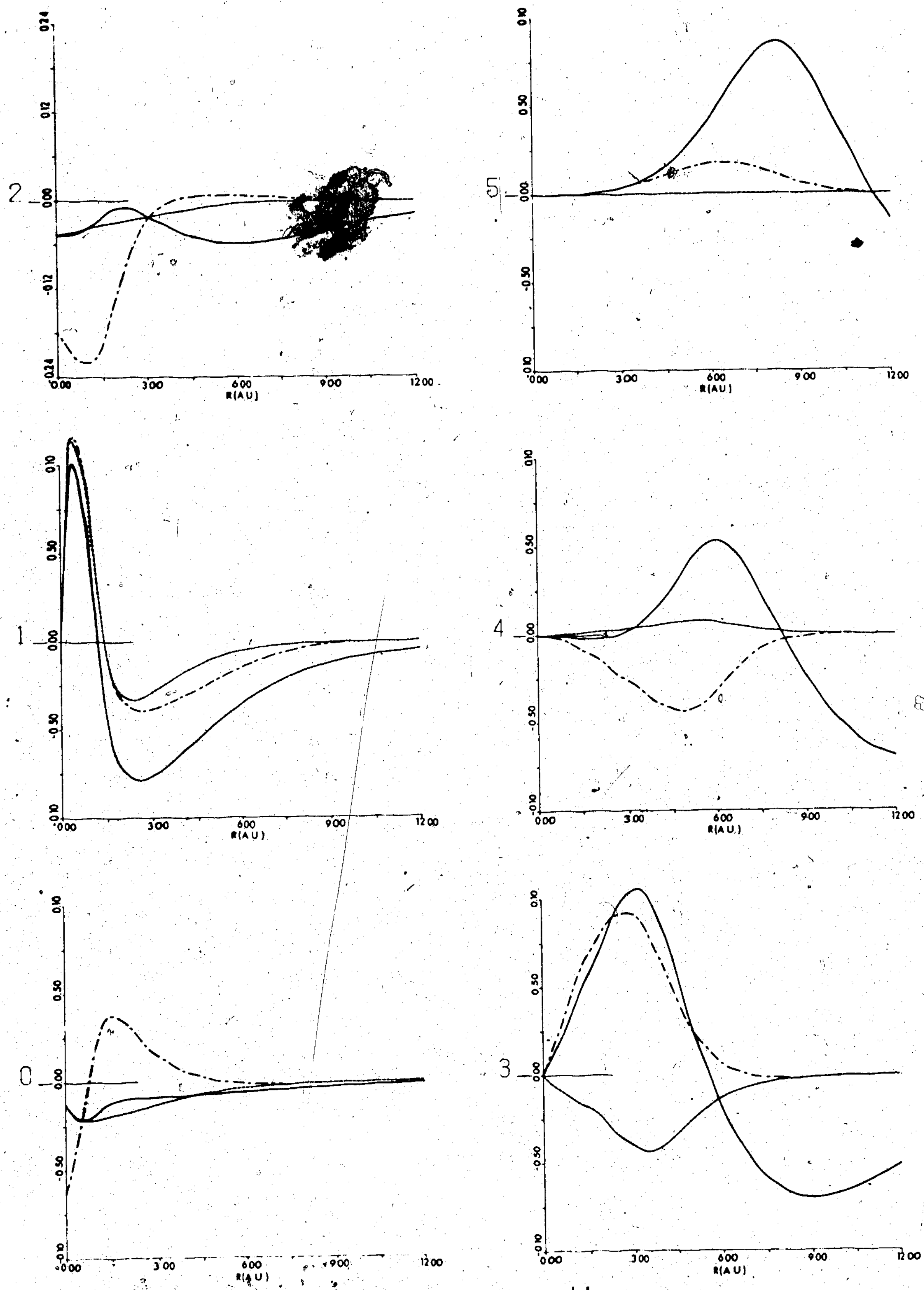

Figure 27. $\langle 0.5L'0|H(\mathrm{RAD})|210\rangle$, HeH^{++}, $L' = 0(1)5$

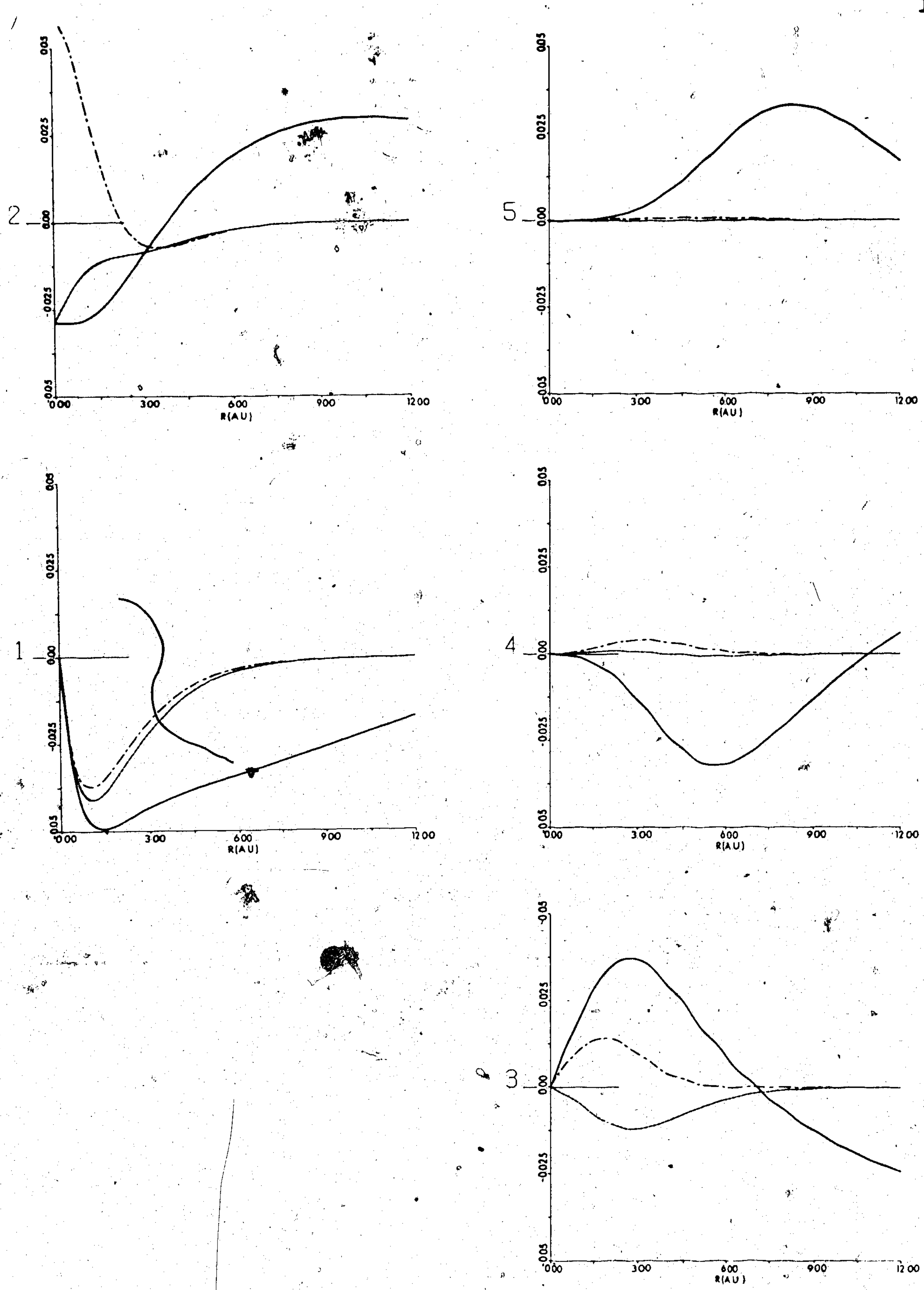

Figure 28. $\langle 0.5L'1|H(RAD)|211\rangle$, HeH^{++}, L' = 1(1)5

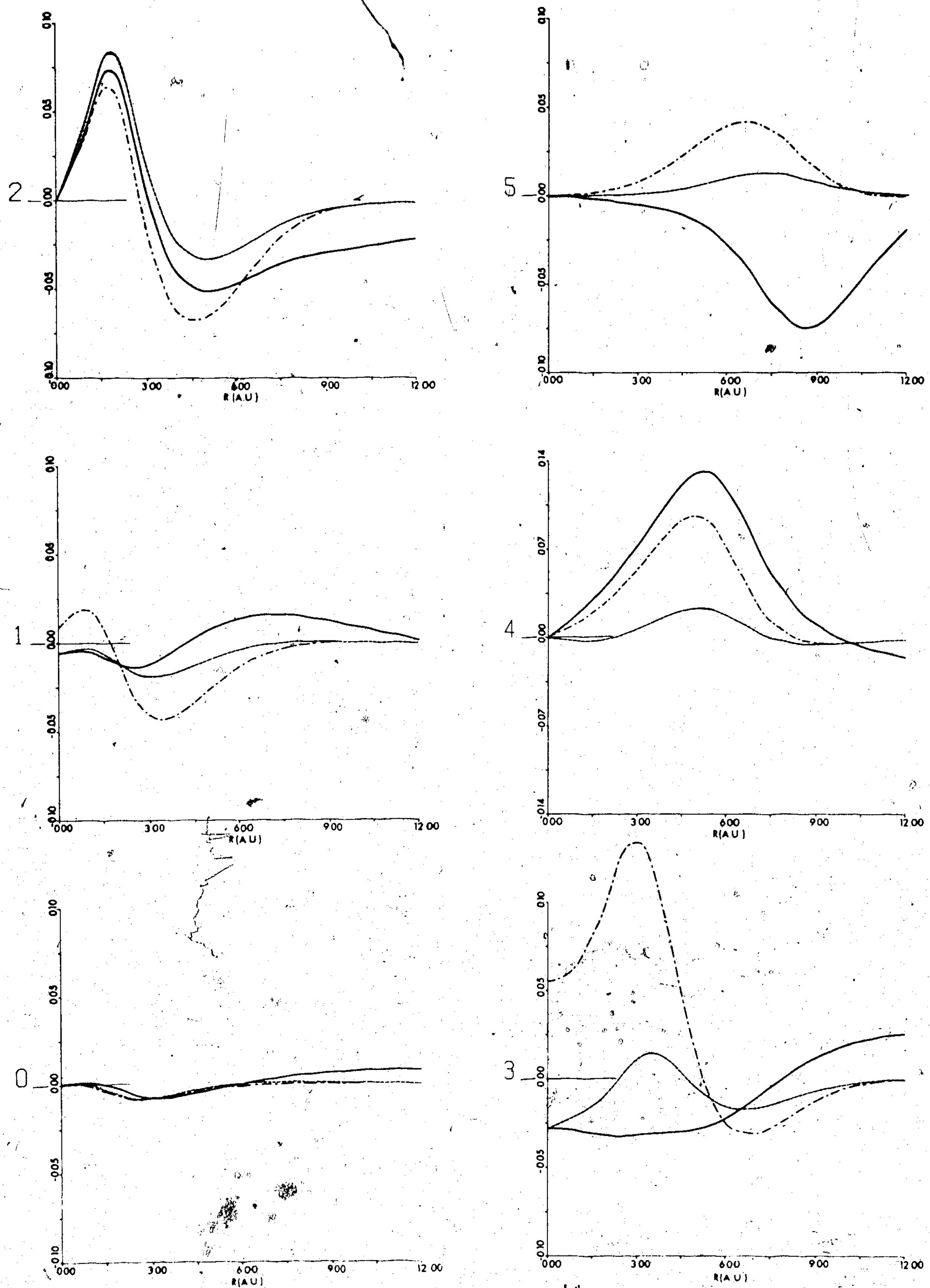

Figure 29. <0.5L'0|H(RAD)|320>, HeH^{++}, L' = 0(1)5

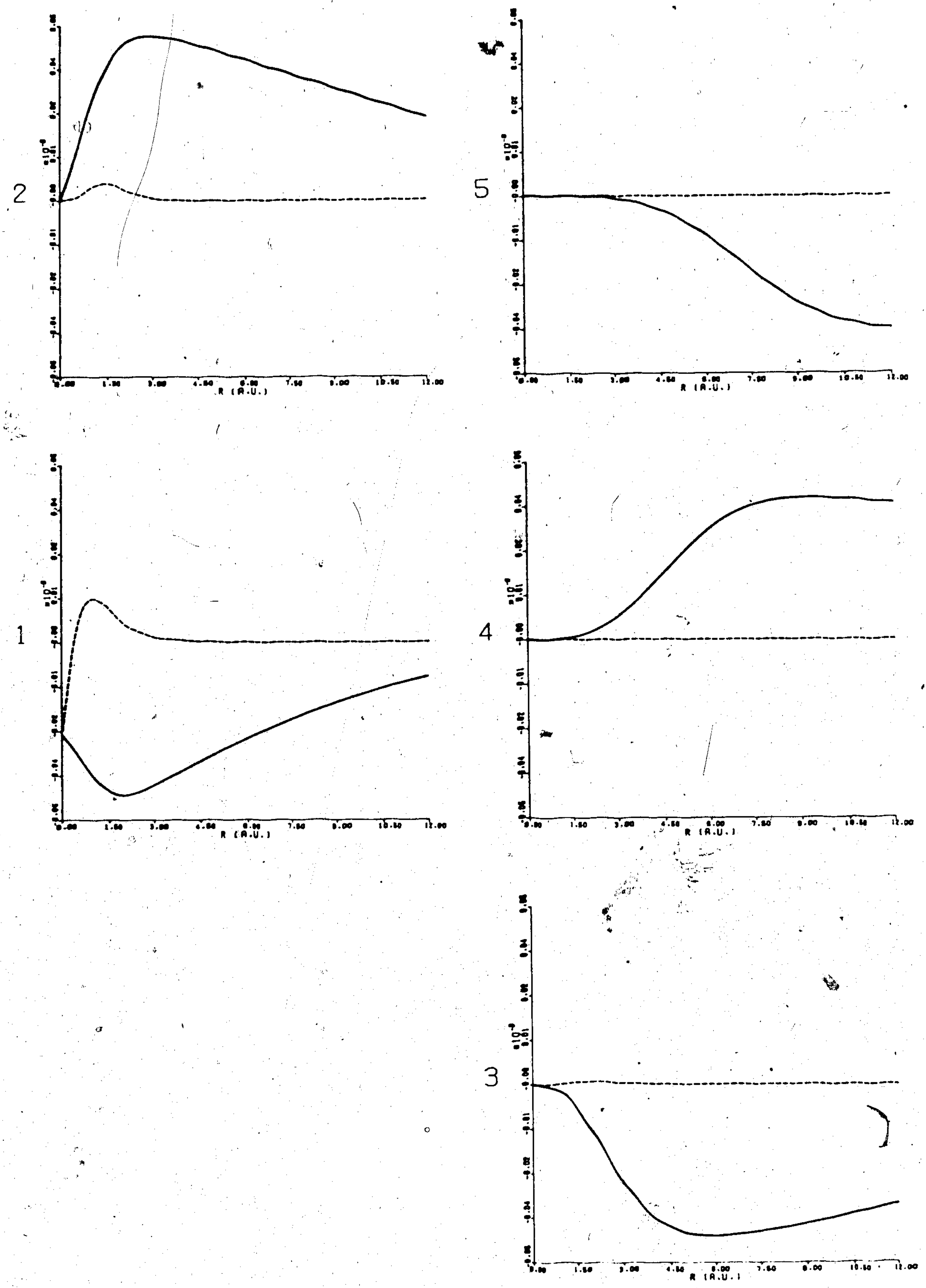

Figure 30. <0.5L'1|H(ANG)|100>, HeH^{++}, L' = 1(1)5

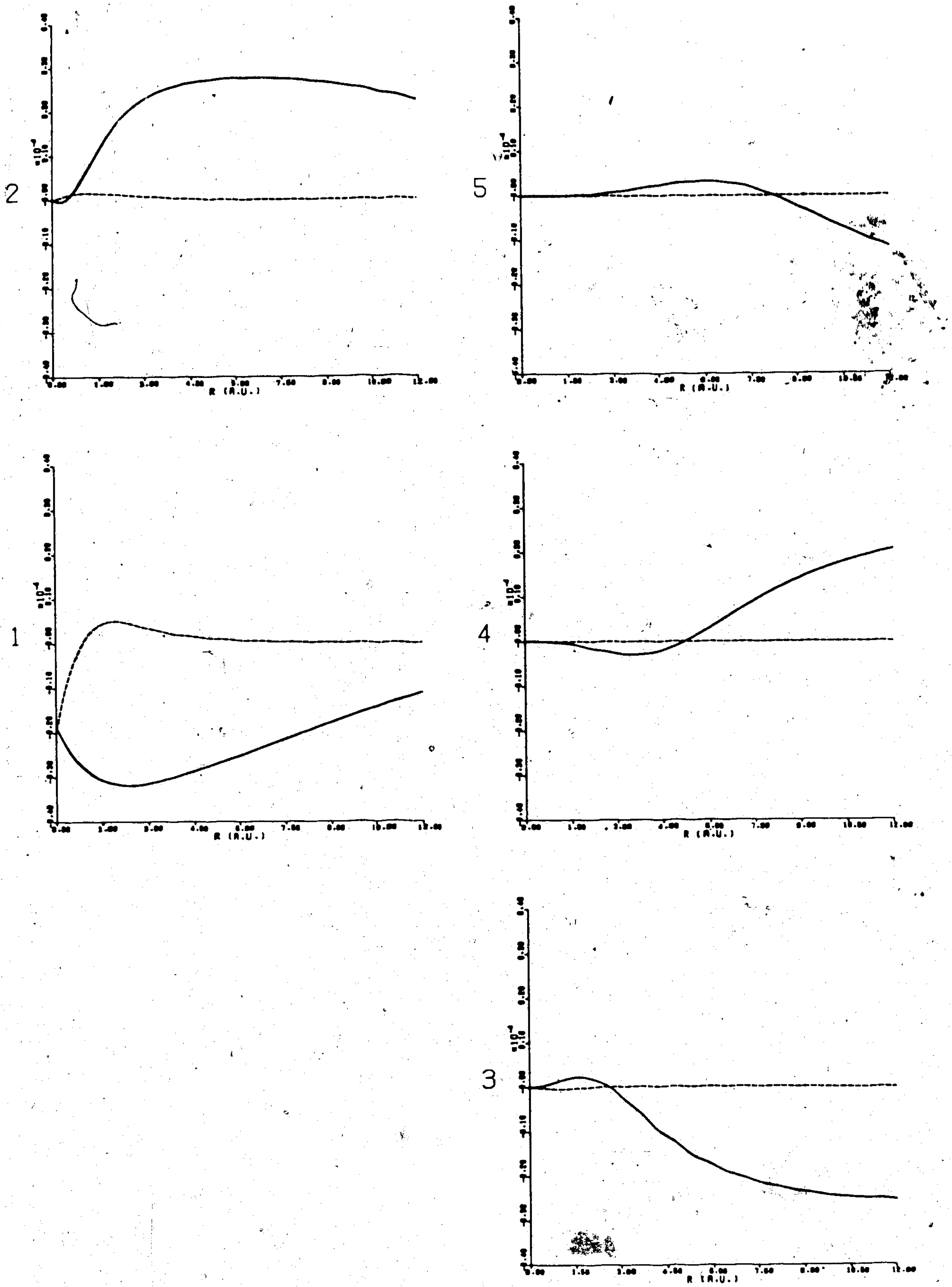

Figure 31. <0.5L'1|H(ANG)|200>, HeH^{++}, L' = 1(1)5

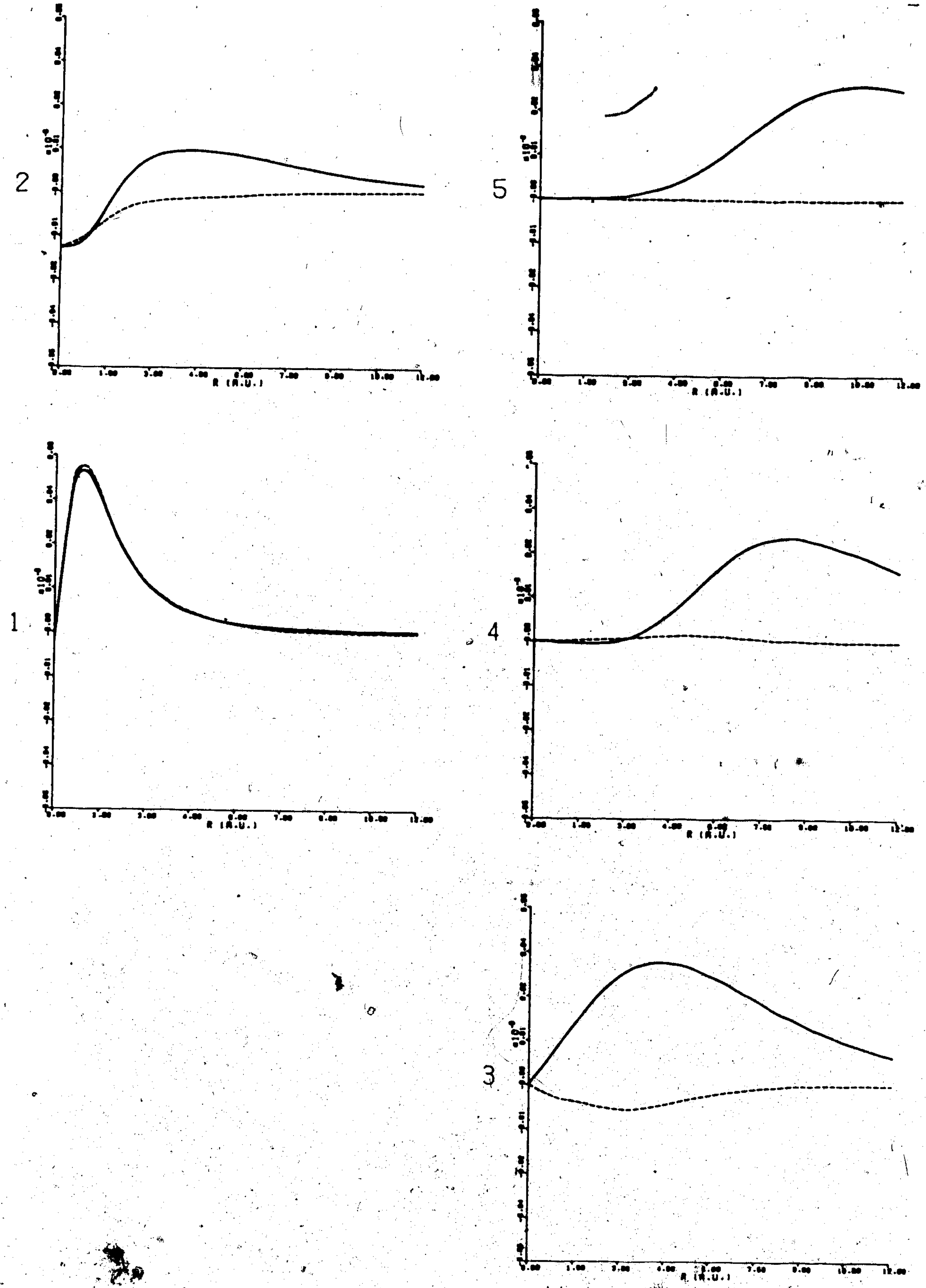

Figure 32. <0.5L'1|H(ANG)|210>, HeH^{++}, L' [illegible].5

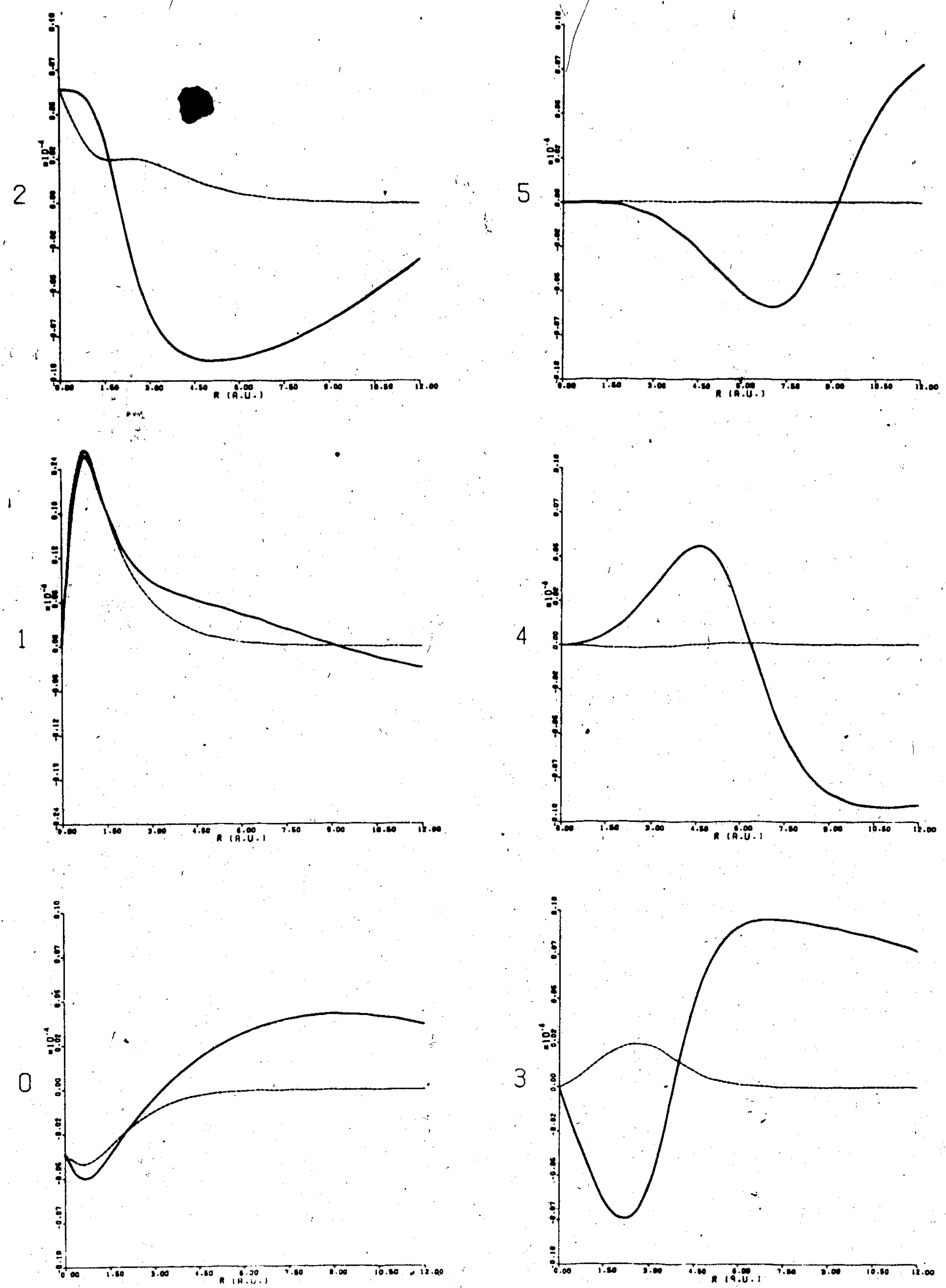

Figure 33. <0.5L'0|H(ANG)|211>, HeH^{++}, L' = 0(1)5

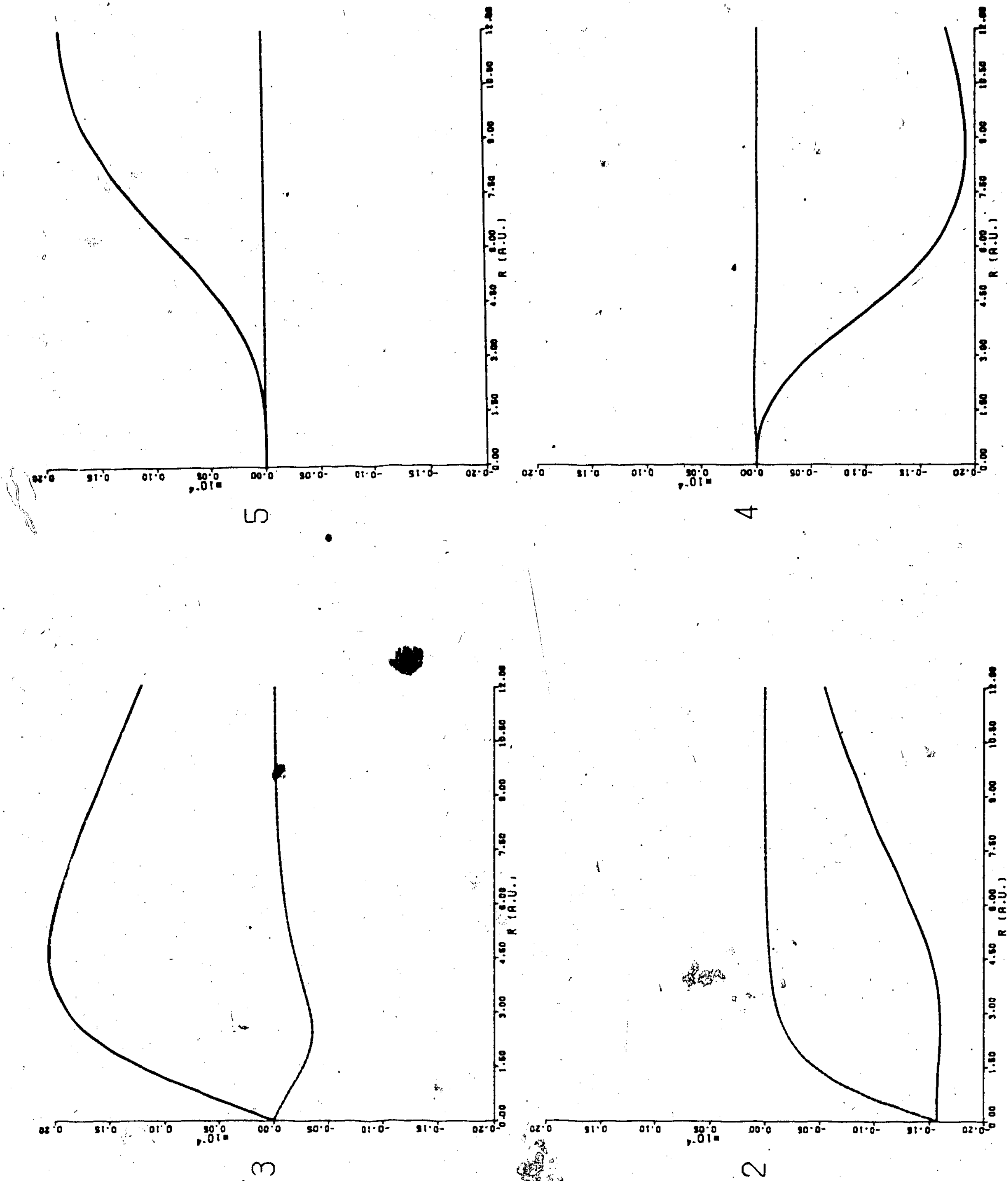

Figure 34. <0.5L'2|H(ANG)|211>, HeH^{++}, L' = 2(1)5

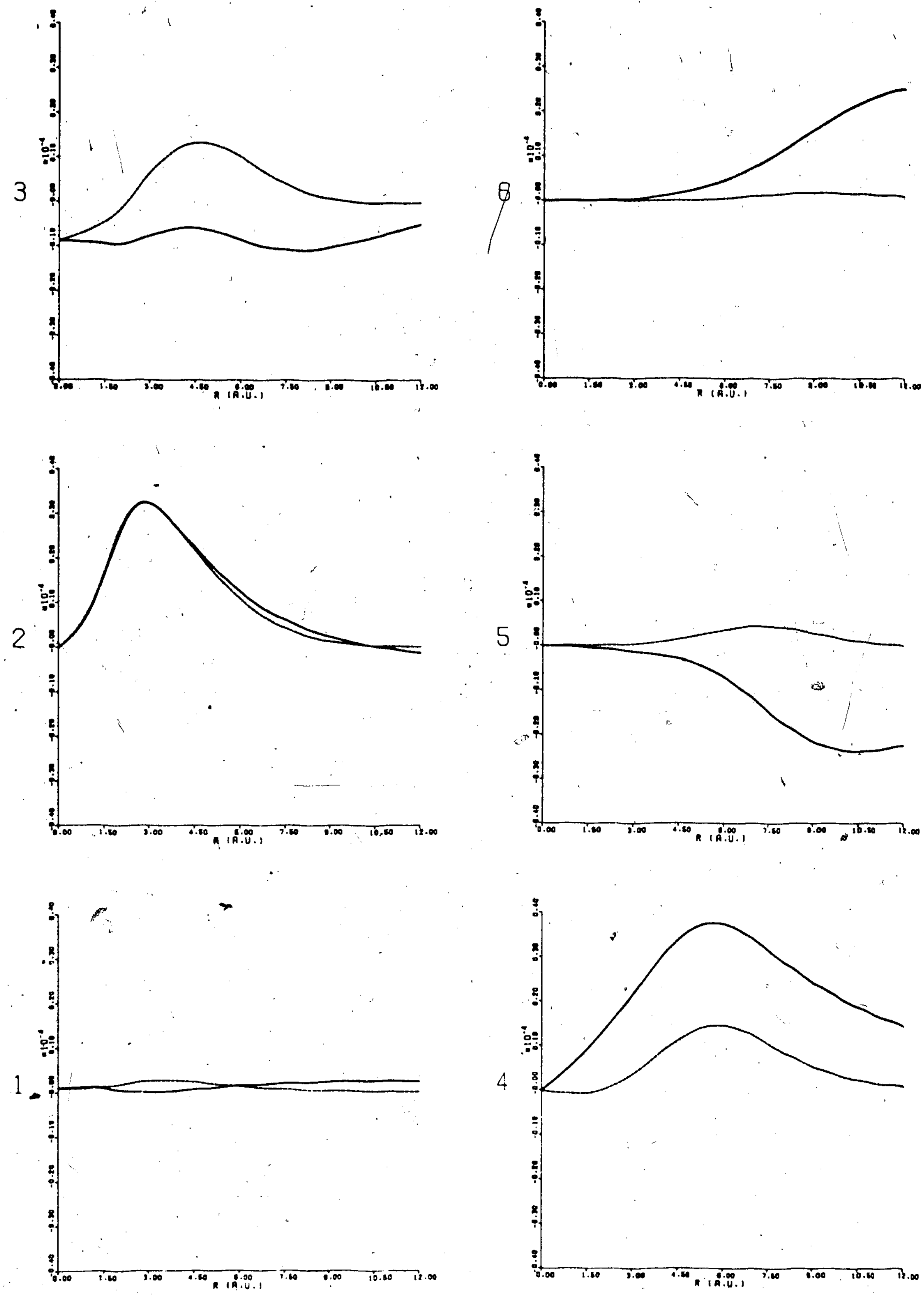

Figure 35. <0.5L'1|H(ANG)|320>, HeH^{++}, L' = 1(1)6

which are obtained using the simple, Bates-McCarroll[3] switching functions ($f_n = +1$, for asymptotic "B" states; and $f_n = -1$, for "A" states). As I noted above, this simple choice gives excellent results for the 1sσ and 2sσ states (figures 25 and 26) at all distances. For the other states, this choice gives results in agreement with those using "optimum" switching functions, at large distances only. For intermediate distances, the resulting couplings are often larger than the uncorrected pss couplings. This is especially true for states like 2pσ, which have significant molecular character (figure 27). These comparisons show that, in such cases, the more elaborate description of switching functions given here is really necessary to describe continuum couplings well. This will probably also be true for couplings between discrete states.

D. Discussion

1. Summary

Using switching functions to describe the effects of electron translation in discrete molecular states, I have shown empirically that (1) the corrected nonadiabatic couplings from these states to the continuum are generally very sensitive to the detailed form of the switching function; (2) with a suitable choice of f, the corrected couplings to all higher partial waves are at least three orders of magnitude smaller than the corresponding uncorrected pss couplings, and the range and magnitude of the remaining couplings are also reduced greatly; and (3) the choice of the switching function which produces this cancellation is independent of continuum state characteristics and of the type of coupling involved, but does depend on the initial discrete state. The results provide strong evidence that the switching function approach to translation factor corrections has a sound physical basis: systematic reductions by several orders of magnitude are not fortuitous. This confirms earlier findings, and extends them to additional discrete states and also to asymmetric systems. The results are significant in two different contexts.

2. Ionisation

First, as was the intent in reference 2, the corrected couplings to continuum states can be used to compute physically sensible impact ionisation cross sections. The rationale for choosing switching functions to minimise continuum couplings has been described previously by Thorson et al.[1c,2a] They argued that (1) ionisation cross sections can be computed by a first-order perturbation approximation; (2) if the cross sections are small (i.e., if coupling is weak), one should choose a zero-order basis set for which the first-order couplings are as small as possible; and (3) one can look upon the "optimisation" calculations as a kind of heuristic variational method. This argument is intuitive, and it is *not* based on any formal variational principle; there is no principle which states that the best zero-order basis is the one which minimises the first-order T-matrix (although, in the case of weak coupling, this is certainly plausible). Note also that minimising the first-order *couplings* does not necessarily minimise the first-order *transition probabilities* (the transition probability is essentially $|\int^{\infty}$ matrix element $\times \exp\{-i\int^{t}\Delta\varepsilon\ dt'/h\}\ dt|^{2}$). Of course, if one reduces a matrix element by a factor of 10^{3}, it is hard to argue that the corresponding T-matrix element is not similarly reduced. Finally, one may ask whether, in fact, first-order perturbation theory provides an adequate description of impact ionisation. The whole question of the convergence of perturbation expansions is extremely complicated, but there are reasons for believing that the "off-shell" contributions from the *second-order* terms may well be important.[57]

Although the impact ionisation theory is based on intuitive ideas, the figures given here and in reference 2 show that orders of magnitude differences will exist between ionisation cross sections computed using uncorrected pss theory, and those computed using the corrected matrix elements. These differences are exaggerated by the fact that the efficiency of ionisation depends very strongly on the effective ionisation potential in the region of coupling.[2b,58] In the $1s\sigma_g$ state of H_2^+, for example, the ionisation potential at short distances is significantly larger than the asymptotic value, and the ionisation cross section is dominated by the contribution of any couplings at distances greater than 2 to 4 au. In pss theory, these contributions are very large, and almost entirely spurious.

Figures 25 to 29 suggest that ionisation cross sections for HeH^{++} computed using the simple asymptotic switching functions, $f_n = \pm 1$, may agree more closely with those computed using the "optimum" f_n's; indeed, the $1s\sigma$ and $2s\sigma$ cross sections should be essentially the same in each case. On the other hand, substantial differences should exist for "molecular" states like $2p\sigma$ (ionisation of H(1s) by He^{++}). Of course, I think that the more elaborate, "optimum" switching functions are the ones appropriate for such cases.

3. Close-coupling

a. Comparison with pss-type Theories

Since the examination of continuum couplings is giving information about the bound state f_n's, the results also have some implications for the selection of switching functions for general close-coupling problems. However, before discussing these, I should first emphasise the distinction between close-coupling formulations which correctly take account of electron translation (switching function theories), and those which do not do so (pss-type theories). This distinction is important for both formal and practical reasons.

I pointed out earlier that any arbitrarily chosen set of switching functions gives a formally valid theory of close-coupling. Moreover, by taking particular choices for the f_n's, nearly all existing theories which take account of electron translation can be accomodated as special cases of such a formulation. Provided the basis used is large enough, the resulting detailed cross sections are guaranteed to be correct and independent of the choice of switching functions. No such guarantees can be given for pss theory, because the basis functions do not satisfy asymptotic scattering boundary conditions. Neither can they be given for modifications which take some fixed point (e.g., the target, or projectile, nucleus) as the reference origin for electron co-ordinates. This is true even though the results may converge numerically, as the number of close-coupled states considered is increased.

Even if we leave aside the question of formal validity, the uncorrected theories are computationally inconvenient. As the figures show for continuum couplings, there are many large, long-ranged matrix elements, and this is also the case for couplings between discrete states. The corrected couplings can be greatly reduced in size and range, even with a very simple switching function. This is an important practical advantage, since computer time is often a limiting factor in close-coupling studies.

Recently, Winter and Lane[20] have described a very thorough treatment of slow collisions in the HeH^{++} system, following an earlier study by Piacentini and Salin.[19] In both studies, the objective is the calculation of the total charge-exchange cross section for He^{++} + H(1s) collisions. Both note the problem of translation factors and their effects, but use the target (H) nucleus as the fixed origin of electron co-ordinates. This ensures that boundary conditions are satisfied for all scattering states in the target channel, but not for those in the He^+ channel. The total capture cross section can be found from probability conservation. Winter and Lane[20] remark that they did not calculate cross sections for individual transitions, because their treatment does not fully take account of translation factor corrections. They include up to 20 discrete states, and present pictures of many of the matrix elements obtained in this formulation.

Choosing the proton as a fixed reference origin is equivalent to taking $f_n = +1$, for all states, i.e., it is not a switching function. Matrix elements coupling states which are asymptotically in the He^+ channel behave like pss matrix elements; those involving states in the H channel are asymptotically well-behaved, but are fairly large at finite distances. Using a switching function formulation, most of these couplings can be greatly reduced in size and range.

b. Comparison with other Switching Functions

Finally, we may consider the respective merits of elaborate "molecular" switching functions (like those determined here), and the simpler choices, $f_n = \pm 1$ (to which ours reduce as $R \to \infty$), for use in close-coupling calculations. Although the whole subject of switching functions needs more study before this question can be resolved, some relevant points are suggested by this work.

(1) As I have pointed out, the behaviour of couplings to the continuum "selects" optimum switching functions which are precisely defined. Moreover, they are functions only of the initial discrete state, and they differ significantly from the simple forms only when the corresponding state, $|n\rangle$, is genuinely "molecular." It seems very likely that the variation of the switching finction is reflecting that molecular character.

(2) In a close-coupling calculation, the basis is truncated to a finite ~~set~~ of molecular electronic states, and couplings to states outside that manifold are ignored. In particular, couplings to the continuum are neglected, because we know that the ionisation cross sections are small. It is certainly consistent with that neglect to use a formulation in which the theoretical couplings to

the continuum are made as small as possible.

(3) We should recognise that it may be possible to reduce the corrected matrix elements still further, with a more sophisticated form for f_n. However, with the possible exception of the 3dσ state, it is my belief that it will be hard to improve much on the spectacular, three to four orders of magnitude reductions.

(4) It will be interesting to compare the results obtained by Winter and Lane,[20] from their close-coupling study of HeH^{++}, with those obtained from studies using (a) the simple switching functions, $f_n = \pm 1$, and (b) the "optimum" f_n's reported here. In the calculations using switching functions, it will also be possible to compute, and compare, the cross sections for individual transitions.

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APPENDIX

STATE-DEPENDENT SWITCHING FUNCTION FORMULATION

A. Introduction

The derivation of the classical trajectory equations in chapter II assumed that the electron translation factor can be characterised by a single switching function common to all electronic states. It is desirable, however, to extend the theory so that each state has its own, characteristic switching function, f_n. The derivation is quite straightforward, and follows that of chapter II, section C. It will be shown that the new coupled equations have the same form as before, but that the definition of $\underline{A}(R)$ is changed. Although the new correction matrix is no longer Hermitian, the equations still conserve probability, to first-order in the nuclear velocity.

B. Definition of Basis

$$\Phi_n(\vec{r};\vec{R}) = F_n \cdot \phi_n(\vec{r}:\vec{R}) = F_n\, |n\rangle, \qquad \text{(A-1)}$$

where

$$F_n = \exp\{(im/h)\ [\vec{v}.\vec{s}_n - \int^t (1-\lambda^2)v^2 dt'/8]\}, \qquad \text{(A-2a)}$$

$$\vec{s}_n = \tfrac{1}{2}\ (f_n+\lambda)\ \vec{r}_g; \qquad \text{(A-2b)}$$

and $\phi_n(\vec{r};\vec{R})$ is a Born-Oppenheimer electronic wavefunction.

In chapter II, the states, $\Phi_n(\vec{r};\vec{R})$, are orthogonal, but when the switching functions are allowed to be state-dependent, the overlap matrix is no longer diagonal. Let us define $\underline{S}(v)$, the overlap matrix, such that

$$S_{jn}(v) = \langle j|F_j^{*}F_n|n\rangle$$

$$= \langle j|\exp\{(im/h)\ \vec{v}.(\vec{s}_n-\vec{s}_j)\}|n\rangle. \qquad \text{(A-3)}$$

To first order in v, we can write

$$\underline{S}(v) = \underline{1} + \vec{v}.\vec{\underline{\sigma}}; \qquad \underline{S}^{-1}(v) = \underline{1} - \vec{v}.\vec{\underline{\sigma}}, \qquad \text{(A-4)}$$

where

$$\vec{\sigma}_{jn} = (im/h)\ \langle j|(\vec{s}_n-\vec{s}_j)|n\rangle. \qquad \text{(A-5)}$$

C. Classical Trajectory Equations

Assuming that the nuclei follow a classical path, the wavefunction, T, satisfies the time-dependent Schrödinger equation,

$$h_e\, T = ih\, \partial T/\partial t, \qquad \text{(A-6)}$$

and we can write (cf. equation (II-42))

$$T = \sum_n b_n\, F_n\, |n\rangle. \qquad \text{(A-7)}$$

Proceeding exactly as in chapter II, we find that (cf. equation (II-50a))

$$ih\, \underline{S}(v)\, \dot{\underline{b}} = \{\underline{h}(v) + \vec{v}.[\vec{\underline{P}}(v)+\vec{\underline{A}}(v)]\}\, \underline{b}, \qquad \text{(A-8)}$$

where

$$h_{jn}(v) = \langle j|F_j^{*} F_n\, h_e|n\rangle, \qquad \text{(A-9a)}$$

$$\vec{P}_{jn}(v) = -i\hbar \langle j|F_j . F_n\, (\vec{\nabla}_R)_{\vec{r}}|n\rangle, \qquad \text{(A-9b)}$$

and

$$\vec{A}_{jn}(v) = (im/h)\, \langle j|F_j^{*} F_n\, [h_e, s_n]|n\rangle. \qquad \text{(A-9c)}$$

To first order in v, we can write

$$\underline{h}(v) = \underline{\varepsilon} + \vec{v}.\vec{\underline{\eta}}, \qquad \text{(A-10)}$$

where

$$\vec{\eta}_{jn} = (im/h)\ \langle j|(\vec{s}_n - \vec{s}_j)\ h_e|n\rangle, \qquad \text{(A-11a)}$$

and

$$\varepsilon_{jn} = \varepsilon_n(R)\ \delta_{jn}. \qquad \text{(A-11b)}$$

Thus, to first order in v,

$$\underline{S}^{-1}(v)\ \underline{h}(v) = \underline{\varepsilon} + \vec{v}\cdot\{\underline{\vec{\eta}} - \underline{\vec{\sigma}}\ \underline{\varepsilon}\} \qquad \text{(A-12)}$$

$$= \underline{\varepsilon}.$$

Hence, if we multiply equation (A-8) on the left by $\underline{S}^{-1}(v)$, and keep only terms which are first order in v, we find

$$ih\ \dot{\underline{b}} = \{\underline{\varepsilon} + \vec{v}\cdot[\underline{\vec{P}}+\underline{\vec{A}}]\}\ \underline{b}, \qquad \text{(A-13)}$$

where

$$\vec{P}_{jn} = -ih\ \langle j|(\vec{\nabla}_R)_{\vec{r}}|n\rangle, \qquad \text{(A-14a)}$$

$$\vec{A}_{jn} = (im/h)\ \langle j|[h_e, \vec{s}_n]|n\rangle. \qquad \text{(A-14b)}$$

Equations (A-13) are the desired coupled equations. They have the same form as (II-50), but the matrix, $\underline{\vec{A}}$, is now non-Hermitian, and defined by (A-14b). I will now show that probability is conserved, to first order in the nuclear velocity.

D. Conservation of Probability

For probability to be conserved, we require

$$d/dt \langle T|T\rangle = 0. \qquad \text{(A-15)}$$

Using Green's method,[1]

$$ih\, d/dt \langle T|T\rangle = ih\, d/dt \{\underline{b}^{\dagger}\, \underline{S}(v)\, \underline{b}\} \qquad \text{(A-16)}$$

$$= ih\, \{\dot{\underline{b}}^{\dagger}\, \underline{S}(v)\, \underline{b} + \underline{b}^{\dagger}\, \dot{\underline{S}}(v)\, \underline{b} + \underline{b}^{\dagger}\, \underline{S}(v)\, \dot{\underline{b}}\}.$$

If we define

$$\vec{\rho}_{jn} = (im/h) \langle j|\vec{s}_n|n\rangle, \qquad \text{(A-17)}$$

then, to first order in v,

$$\underline{S}(v) = \underline{1} + \vec{v}.\vec{\underline{\sigma}} = \underline{1} + \vec{v}.(\vec{\underline{\rho}} + \vec{\underline{\rho}}^{\dagger}) \qquad \text{(A-18a)}$$

and

$$\vec{\underline{A}} = \underline{\varepsilon}\, \vec{\underline{\rho}} - \vec{\underline{\rho}}\, \dot{\underline{\varepsilon}}. \qquad \text{(A-18b)}$$

Using equation (A-13), we can eliminate $\dot{\underline{b}}$ and $\dot{\underline{b}}^\dagger$ from (A-16), and obtain

$$ih\, d/dt \langle T|T\rangle = b^\dagger\ \{\vec{v}.(\underline{\vec{\sigma}}\ \underline{\varepsilon} - \underline{\varepsilon}\ \underline{\vec{\sigma}}) + ih\ \vec{v}.\vec{\nabla}_R(\vec{v}.\underline{\vec{\sigma}}) + \vec{v}.(\underline{\vec{A}} - \underline{\vec{A}}^\dagger)\}\ \underline{b}, \qquad (A\text{-}19)$$

since both $\underline{\varepsilon}$ and $\underline{\vec{P}}$ are Hermitian matrices. But

$$\underline{\vec{A}} - \underline{\vec{A}}^\dagger = \underline{\varepsilon}(\underline{\vec{\rho}} + \underline{\vec{\rho}}^\dagger) - (\underline{\vec{\rho}} + \underline{\vec{\rho}}^\dagger)\underline{\varepsilon}$$

$$= \underline{\varepsilon}\ \underline{\vec{\sigma}} - \underline{\vec{\sigma}}\ \underline{\varepsilon}; \qquad (A\text{-}20)$$

and hence

$$ih\, d/dt \langle T|T\rangle = \underline{b}^\dagger\ \{ih\ \vec{v}.\vec{\nabla}_R(\vec{v}.\underline{\vec{\sigma}})\}\ \underline{b}, \qquad (A\text{-}21)$$

which is of order v^2.

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