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# High Precision Theoretical Study of $\text{H}_2^+$

by

Mark Michael Cassar

A Dissertation  
Submitted to the Faculty of Graduate Studies and Research  
through the Department of Physics  
in Partial Fulfillment of the Requirements for  
the Degree of Doctor of Philosophy at the  
University of Windsor

Windsor, Ontario, Canada

2004

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## Abstract

A study of the hydrogen molecule-ion  $\text{H}_2^+$  is presented. The purpose is to show that a carefully modified, doubled basis set in the standard Hylleraas coordinates provides an excellent, yet straightforward, description of this ion without recourse to approximation methods. Three non-linear parameters are used so that distance scales may be set independently for all three radial coordinates  $r_1$ ,  $r_2$  and  $r_{12}$ . Vibrational modes are effectively accounted for by including only high powers of the inter-proton coordinate  $r_{12}$ . High precision variational calculations are carried out for the  $1\ ^1S$  ground state, and the first two excited states –  $2\ ^1S$  and  $2\ ^3P$ .

*for Bonnie, Drew, Kurt, and Reed*

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# 1 Introduction

The main goal of this dissertation is to extend previous work on one-center, three-body quantum systems [1] to include the two-center system of the hydrogen molecule-ion  $H_2^+$ ; thereby developing a systematic way of calculating, to high-precision, the energy eigenvalues and corresponding eigenfunctions for a wide range of three-body atomic systems. It should be emphasized that such an approach may be formulated without invoking the Born-Oppenheimer approximation [2]. For three-body systems where two of the constituent particles are much more massive than the third, this approximation is equivalent to the infinite nuclear mass case for systems such as helium, where only one particle is more massive than the other two.

In a general way, one may establish a hierarchy of three-body systems that should be described by the same quantum theory. We may thus classify these microscopic systems as falling into (i) the atomic regime, where one particle is much more massive than the other two (one-center), or (ii) the molecular regime, where one particle is much less massive than the other two (two-center). In this scheme we can clearly see that  $H^-$ , consisting of a proton and two electrons ( $p^+e^-e^-$ ), is on the atomic side, while  $H_2^+$ , containing two protons and one electron ( $p^+p^+e^-$ ), is on the molecular side. This distinction is, however, not absolute, since a system such as  $Ps^-$ , consisting of one positron and two electrons ( $e^+e^-e^-$ ), resides on the cusp between these two regimes.

In treating all these systems in the same way, we anticipate that the states of  $H^-$  should transform into the states of  $H_2^+$ , thereby allowing a one-to-one mapping of atomic states onto molecular states. The parameter that would govern this continuous evolution of states must be the atomic mass ratio  $\mu/\mathcal{M}$ , where  $\mu$  is the reduced mass for the system [see Eq. (19)] and  $\mathcal{M}$  is the so-called nuclear mass, since the Hamiltonians for all these systems are alike except for this ratio. Each infinitesimal increment of  $\mu/\mathcal{M}$  would be accompanied by an optimization of all nonlinear parameters; and thus, the nonlinear parameters should be smooth functions of  $\mu/\mathcal{M}$ .

The one feature that all three-body systems share is that they present the theoretician with a problem having no known exact solution. And thus, one continually seeks new and increasingly accurate means of approximation. Over the years, variational methods have proven to be one of the most powerful approaches to such problems. In the simplest of terms, one wishes to find the energy levels for the atomic system in question. In order to do this, one searches for solutions of the corresponding Schrödinger equation. The bound state solutions for such systems are quantized, and as such correspond to the eigenvalues of the equation.

This work applies the variational principle to solve the above problem for the nonrelativistic energy eigenvalues for the  $1^1S$ ,  $2^1S$ , and  $2^3P$  states of  $H_2^+$ . The wave functions used in the calculations are constructed so that they mirror the physical nature of the problem in two important ways: they allow distance scales along the three radial coordinates to be set independently; and they accurately represent the vibrational modes of the system. Such characteristics are absolutely necessary for two-center systems, i.e. when the atomic mass ratio is on the order of one.

## 2 Historical Survey

The hydrogen molecule-ion, or  $\text{H}_2^+$ , has been a system of interest since its discovery in 1907 by J. J. Thomson [3]. Along with helium, this ion was one of the first stumbling blocks for the old quantum theory of Bohr and Sommerfeld [4, 5, 6, 7]. And, as such, it became one of the preliminary three-body quantum systems studied under the new wave mechanics of Schrödinger [8]. The early success of Schrödinger's theory in 1927, when applied to  $\text{H}_2^+$  [9], has been continuously built upon for almost 80 years. During these years various methods and approaches have been developed and applied to this ion: variational methods, variation-perturbation methods, artificial channel methods, and transformed Hamiltonian methods.

A complete history of the hydrogen molecule-ion would not be wholly pertinent to the work at hand; and therefore, we refer the reader to a few reviews (and references therein) in the literature [10, 11, 12] for details of the development of both theory and experiment. We, however, pick up the story in 1995, after the more general review of the subject by Leach and Moss [13].

In 1995, Frolov carried out a variational calculation for the ground state of the hydrogen molecule-ion. The wave function he used was written as

$$\Psi = \frac{1}{2}(1 \pm \hat{P}_{12}) \sum_{i=1}^N \sum_{l_1} C_i e^{-\alpha_i r_{32} - \beta_i r_{31} - \gamma_i r_{21}} e^{i\delta_i r_{32} + i e_i r_{31} + i f_i r_{21}} Y_{LM}^{l_1 l_2}(r_{31}, r_{32});$$

the  $Y_{LM}^{l_1 l_2}(r_{31}, r_{32})$  are Schwartz or bipolar harmonics,  $i$  is the imaginary unit. The set of nonlinear parameters are generated in a so-called quasi-random manner from a set of real intervals, as follows:

$$\begin{aligned} \alpha_i &= \left[ \frac{1}{2} i(i+1) \sqrt{2} \right] (A_2 - A_1) + A_1, \\ \beta_i &= \left[ \frac{1}{2} i(i+1) \sqrt{3} \right] (B_2 - B_1) + B_1, \\ \gamma_i &= \left[ \frac{1}{2} i(i+1) \sqrt{5} \right] (C_2 - C_1) + C_1, \\ \delta_i &= \left[ \frac{1}{2} i(i+1) \sqrt{7} \right] (D_2 - D_1) + D_1, \\ e_i &= \left[ \frac{1}{2} i(i+1) \sqrt{11} \right] (E_2 - E_1) + E_1, \\ f_i &= \left[ \frac{1}{2} i(i+1) \sqrt{13} \right] (F_2 - F_1) + F_1, \end{aligned}$$

where  $[x]$  is the fractional part of  $x$ . Certain restrictions are required in order that the wave function remain square integrable. This method produced an energy<sup>1</sup> of  $-0.597\,139\,053\,69$ .

Ackermann and Shertzer [16], in 1996, used an adaptive finite element method where the domain of the wave function is divided into tetrahedra, each serving as the domain of a local polynomial basis set. The error  $\delta E$  in the energy is minimized on each local domain; and the method is variational in the sense that the total energy is a true upper bound. In any domain

$$\Psi \approx \tilde{\Psi}_{\text{FEM}}^{(p)} = \sum_{i=0}^M C_i \phi_i^{(p)},$$

where the  $\phi_i^{(p)}$  are Lagrange polynomials of order  $p$ . In this way the ground state energy was found to be  $-0.597\,139\,062\,3$ .

Rebane and Filinsky carried out a detailed variational calculation in 1997 for symmetric three-body systems (trions) of varying masses. A parametric dependence of the minimum eigenvalue of the Hamiltonian on the particle masses was determined. Precision values were then calculated for various systems within a variational approach which implemented a basis of Laguerre functions in perimetric coordinates. Explicit formulas were constructed to determine the energies of the ground states of all such Coulomb systems with unit charges and arbitrary masses. Application of this method to  $\text{H}_2^+$  gave a ground state energy of  $-0.597\,139\,063\,123\,40$ .

Grémaud *et al.* [19] proposed a method of calculating the energy eigenvalues for  $\text{H}_2^+$  based on three guiding principles: (i) the members of the basis set are reasonably close to the eigenstates; (ii) the Hamiltonian matrix has only a small number of non-zero elements; and (iii) these matrix elements are easy to calculate. They used the perimetric coordinates

$$\begin{aligned} x &= r_1 + r_2 - r_{12}, \\ y &= r_1 - r_2 + r_{12}, \\ z &= -r_1 + r_2 + r_{12}. \end{aligned}$$

---

<sup>1</sup>Unless noted otherwise, atomic units will be used throughout this work [14, 15].

The basis members were taken as products of Laguerre polynomials:

$$\Phi(x, y, z) \propto \sqrt{\alpha} \beta L_{n_x}(\alpha x) e^{-\alpha x/2} L_{n_y}(\beta y) e^{-\beta y/2} L_{n_z}(\beta z) e^{-\beta z/2}.$$

The energies, obtained variationally, for the first two rotationless states were found to be  $-0.597\,139\,063\,123(1)$  and  $-0.587\,155\,679\,212(1)$ . The uncertainties are estimated by studying the variations of the energy in the vicinity of the optimum value of  $\alpha$ .

Bhatia, in 1998, attempted a variational calculation of the ground state energy using a Hylleraas basis, with two nonlinear parameters, written as (for  $S$ -states)

$$\Psi_0 = e^{-\alpha(r_1+r_2)} e^{-\beta r_{12}} \sum_{l,m,n=0}^{\Omega_0} C_{lmn} r_1^l r_2^m r_{12}^n \pm (\text{exchange}).$$

The resulting energy was the very poor value  $-0.596\,46$ . The reason for this is that the above wave function is capable of describing the correlations between the nuclei and the electron but not the correlation between the nuclei, which is known from the Born-Oppenheimer approximation to be described by a Gaussian-like function. To account for this, he modified the wave function so that it would approximate this Gaussian behaviour along the  $r_{12}$  coordinate:

$$\Psi = r_{12}^N \Psi_0,$$

where  $N$  is large and  $\beta \approx N/2$ . In a given calculation,  $\Omega_0 + N$  was held constant as  $\Omega_0$  was increased. For  $\Omega_0 = 13$  and  $N = 10$ , i.e. 308 terms in the basis, the improved ground state energy was  $-0.597\,138\,955$ . Bhatia and Drachman [21] presented a more thorough explanation of this approach in 1999, but did not extend the calculation to determine a lower energy.

Frolov in 1999 used a so-called universal exponential expansion to calculate the ground state energy. The wave function was of the following form:

$$\Psi(N) = \frac{1}{2} (1 \pm \hat{P}_{12}) \sum_{i=1}^N C_i e^{-\alpha_i r_{32} - \beta_i r_{31} - \gamma_i r_{21}} e^{-\imath f_i r_{21}},$$

where  $r_{21}$  is the internuclear coordinate,  $\hat{P}_{12}$  is the permutation operator,  $C_i$  are linear parameters,  $\imath$  is the imaginary unit and  $\alpha_i$ ,  $\beta_i$ ,  $\gamma_i$ , and  $f_i$  are

nonlinear parameters. He uses a two-stage procedure in which

$$\Psi(N) = \Psi_1(N_0) + \Psi_2(N - N_0)$$

the nonlinear parameters for  $\Psi_1$  are optimized while those for  $\Psi_2$  are chosen in a so-called quasi-random manner as described above. He determined a value of  $-0.597\,139\,063\,107\,6$  when  $N_0 = 100$  and  $N = 500$ .

In 1999, Taylor *et al.* [22] carried out a nonadiabatic study using variational basis sets. They used wave functions of the form

$$\Psi_{\Lambda p N}(\lambda, \mu, \chi, R) = \sum_{s=1}^S k_s \Phi_{bc}^{\Lambda p}(\lambda, \mu, \chi) \chi_d(R),$$

where the summation is over combinations of  $b$ ,  $c$  and  $d$ ,

$$\Phi_{bc}^{\Lambda p}(\lambda, \mu, \chi) = (\lambda^2 - 1)^{|\Lambda|/2} L_b^{|\Lambda|}[\alpha(\lambda - 1)] e^{-\frac{1}{2}\alpha(\lambda-1)} P_c^{|\Lambda|}(\mu) e^{i\Lambda\chi}$$

is the electronic part of wave function and

$$\chi_d(R) = (1/R)(\gamma R)^{(\beta+1)/2} L_d^\beta(\gamma R) e^{-\frac{1}{2}\gamma R}$$

is a vibrational basis function;  $N$  is a rotational quantum number. The prolate spheroidal coordinates  $(\lambda, \mu, \chi)$  are given by  $\lambda = (r_1 + r_2)/R$ ,  $\mu = (r_1 - r_2)/R$ , with  $r_i$  being the distance of the electron from the  $i$ th proton, and  $R$  the inter-protonic coordinate, and  $\chi$  is the angle of rotation about the inter-protonic axis; the  $L_{|\Lambda|}^b$  and  $L_d^\beta$  are associated Laguerre polynomials. The wave functions consist of three sectors: two electronic sectors with indices  $b$  and  $c$  and nonlinear parameter  $\alpha$  and one vibrational sector with index  $d$  and governed by the nonlinear parameters  $\beta$  and  $\gamma$ . Calculations were done for the ( $v = 0, N = 0$ ) ground state, the first excited rotationless ( $v = 1, N = 0$ ) state and the first rotationally excited ( $v = 0, N = 1$ ) state with the results  $-0.597\,139\,063\,123\,9(5)$ ,  $-0.587\,155\,679\,213\,6(5)$ , and  $-0.596\,873\,738\,832\,8(5)$ , respectively.

Moss [23], also in 1999, reports values based on two approaches – one variational and the other a scattering method – developed in [25, 24]. He quotes a variational value of  $-0.597\,139\,063\,123\,4$  for the ground state and



Table 1: Comparison of the nonrelativistic energies for the three lowest states of  $H_2^+$ .

Author	Year	Reference	Energy
$1^1S$			
Rebane and Filinsky	1997	[17]	-0.597 139 063 123 40
Saavedra <i>et al.</i>	1998	[18]	-0.597 139 063 123
Grémaud <i>et al.</i>	1998	[19]	-0.597 139 063 123(1)
Taylor <i>et al.</i>	1999	[22]	-0.597 139 063 123 9(5)
Moss	1999	[23]	-0.597 139 063 123 4
Korobov	2000	[26]	-0.597 139 063 123 405 074
Hilico <i>et al.</i>	2000	[27]	-0.597 139 063 123 40(1)
Bailey and Frolov	2002	[31]	-0.597 139 063 123 405 074 83
Yan <i>et al.</i>	2003	[34]	-0.597 139 063 123 405 074 5(4)
$2^1S$			
Grémaud <i>et al.</i>	1998	[19]	-0.587 155 679 212(1)
Moss <i>et al.</i> (variational)	1999	[25, 23]	-0.587 155 679 212 7
Moss <i>et al.</i> (transf. Ham.)	1999	[24, 23]	-0.587 155 679 212 8
Taylor <i>et al.</i>	1999	[22]	-0.587 155 679 213 6(5)
Hilico <i>et al.</i>	2000	[27]	-0.587 155 679 212 75(1)
$2^3P$			
Taylor <i>et al.</i>	1999	[22]	-0.596 873 738 832 8(5)
Moss	1999	[23]	-0.596 873 738 832 8
Hilico <i>et al.</i>	2000	[27]	-0.596 873 738 83(1)
Yan <i>et al.</i>	2003	[34]	-0.596 873 738 832 764 733(1)

-0.587 155 679 212 7 for the first excited  $L = 0$  state, where a Fues vibrational basis was used. The scattering method incorporated the use of a transformed Hamiltonian, and the basis functions

$$\phi = (2\pi)^{-1} e^{-\alpha(\lambda-1)/2} L_{m_i}^{(o)}[\alpha(\lambda-1)] P_{n_i}(\mu),$$

where  $\lambda$  and  $\mu$  are the prolate spheroidal coordinates, the  $L_{m_i}^{(o)}$  and  $P_{n_i}$  are an associated Laguerre and a Legendre polynomial, respectively; and  $R = r_{12}$ , the inter-protonic distance, is taken as a scattering parameter. With this technique, for the same states, he found the energies -0.597 139 063 123 5 and -0.587 155 679 212 8.

In 2000, Korobov [26] used the expansion

$$\begin{aligned} \Psi_0 = & \sum_{i=1}^{\infty} \{U_i \Re[\exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12})] \\ & + W_i \Im[\exp(-\alpha_i r_1 - \beta_i r_2 - \gamma_i r_{12})]\} \mathcal{Y}_{l_1 l_2}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2), \end{aligned}$$

where  $\alpha_i$ ,  $\beta_i$  and  $\gamma_i$  are complex parameters chosen in a so-called pseudo-random manner according to

$$\alpha_i = \left\lfloor \frac{1}{2}i(i+1)\sqrt{p_\alpha} \right\rfloor [(A_2 - A_1) + A_1] + i \left\{ \left\lfloor \frac{1}{2}i(i+1)\sqrt{q_\alpha} \right\rfloor [(A'_2 - A'_1) + A'_1] \right\},$$

where  $\lfloor x \rfloor$  designates the fractional part of  $x$ , the  $p_\alpha$  and  $q_\alpha$  are some prime numbers and the real variational parameters  $A_1$ ,  $A_2$  and  $A'_1$ ,  $A'_2$  are the end points of real intervals and need to be optimized. A variational calculation for the ground state energy, including 2200 terms in the wave function and using multiple precision [32], gave an energy of  $-0.597\,139\,063\,123\,405\,074\,0$ .

Also in 2000, Hilico *et al.* [27] used the wave functions

$$\Psi^{JM} = \sum_{T=-J}^J D_{M,T}^{J*}(\psi, \theta, \phi) \Phi_T^{JM}(R, \rho, \zeta),$$

where angular functions are related to the matrix elements of the rotation operators [28]:

$$D_{M,T}^{J*}(\psi, \theta, \phi) = \sqrt{\frac{2J+1}{8\pi^2}} R_{M,T}^{J*}(\psi, \theta, \phi).$$

They used a variational method, but expressed the wave function in perimetric coordinates in order to take full advantage of the dynamical symmetries offered by the system. The  $\Phi$  in the above expansion are taken as products of Laguerre polynomials in the perimetric coordinates  $x$ ,  $y$ , and  $z$ , where

$$\begin{aligned} R &= \frac{y+z}{2}, \\ \rho^2 &= xyz \frac{x+y+z}{(y+z)^2}, \\ \zeta &= \frac{(y-z)(2x+y+z)}{4(y+z)}. \end{aligned}$$

Energies were calculated for all  $J = 0$  and 1 vibrational levels. Their results for the three lowest states are:  $-0.597\,139\,063\,123\,40$ ,  $-0.596\,873\,738\,83$ , and  $-0.587\,155\,679\,212\,75$ .

The following year, Korobov [29] used a variational method with a wave function describing the ground state of the hydrogen molecule-ion taken in the form

$$\Psi_0 = \sum_{i=1}^{\infty} [C_i \cos(v_i R_{12}) + D_i \sin(v_i R_{12})] e^{-\alpha_i r_1 - \beta_i r_2 - \gamma_i R_{12}} + (\mathbf{r}_1 \leftrightarrow \mathbf{r}_2),$$

with the parameters  $v_i$ ,  $\alpha_i$ ,  $\beta_i$  and  $\gamma_i$  being generated in a pseudo-random manner as outlined above. Truncating this expansion after 800 terms yielded an energy of  $-0.59713906312340(1)$ .

Frolov [30], in 2002, performed an exponential variational calculation in perimetric coordinates. The basis functions he used were written as

$$\psi_i = e^{-\alpha_i u_1 - \beta_i u_2 - \gamma_i u_3} e^{i\delta_i u_1 + i\epsilon_i u_2 + i\zeta_i u_3} Y_{LM}^{l_1 l_2}(r_{31}, r_{32});$$

the  $Y_{LM}^{l_1 l_2}(r_{31}, r_{32})$  are Schwartz or bipolar harmonics,  $i$  is the imaginary unit, and the  $u_1 = x/2$ ,  $u_2 = y/2$ , and  $u_3 = z/2$  are perimetric coordinates. Using 72-116 decimal digit accuracy (using the MPFUN [32] package developed by Bailey) and 2600 terms, he calculated a value for the ground state of  $H_2^+$  equal to  $-0.59713906312340507474$ . In the same year, Bailey and Frolov [31], using the same approach, extended the number of terms to 3500 and then obtained the lower energy value  $-0.59713906312340507483$ .

In 2003, Zong-Chao Yan, Jun-Yi Zhang, and Yue Li [34] carried out a variational calculation for the ground state of  $H_2^+$ . They used a basis set in Hylleraas coordinates of the form

$$\phi_{ijk}(\mathbf{r}_1, \mathbf{r}_2) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2} \mathcal{Y}_{l_1 l_2}^{LM}(\mathbf{r}_1, \mathbf{r}_2).$$

Instead of using the electron as the origin, they chose one of the protons. The reason for this is that they could then effectively represent the vibrational nuclear motion through the  $r_2^j e^{-\beta r_2}$  portion of the wave function,  $j \geq j_{\min} = 35$ . This Gaussian-like simulation of the vibrational modes was pointed out by Bhatia [20], and Bhatia and Drachman [21], in consideration of the Born-Oppenheimer approximation. They included all powers of the coordinates according to

$$i + j + k \leq \Omega,$$

where  $\Omega$  is an integer. Each set of powers  $(i, j, k)$  in the basis set was repeated with eight different values of the nonlinear parameters  $\alpha$  and  $\beta$ . For the ground state energy, using 1330 terms in their expansion, they obtained a value of  $-0.5971390631234050745$ .

## 3 The General Problem

### 3.1 The Schrödinger Equation

All bound state energies and eigenfunctions of an arbitrary, three-body quantum system are found by solving the appropriate Schrödinger equation

$$H\Psi = E\Psi, \quad (1)$$

where the nonrelativistic Hamiltonian  $H$  (in Gaussian units [15]), with respect to some fixed origin (see Fig. 1), is

$$H = -\frac{\hbar^2}{2m_1}\nabla_1^2 - \frac{\hbar^2}{2m_2}\nabla_2^2 - \frac{\hbar^2}{2m_3}\nabla_3^2 + \frac{q_1q_2}{r_{12}} + \frac{q_1q_3}{r_{13}} + \frac{q_2q_3}{r_{23}}, \quad (2)$$

$E$  is a negative eigenvalue and  $\Psi$  is the corresponding eigenfunction. In Eq. (2) we have used the following definitions:

$$r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|,$$

$$\mathbf{r}_i = (x_i, y_i, z_i),$$

and

$$\nabla_i^2 = \frac{\partial^2}{\partial x_i^2} + \frac{\partial^2}{\partial y_i^2} + \frac{\partial^2}{\partial z_i^2}. \quad (3)$$

We may now change from fixed-origin to internal and centre-of-mass coordinates (see Fig. 2), and thereby isolate the centre-of-mass motion. These coordinates are

$$\begin{aligned} \rho_1 &= \mathbf{r}_1 - \mathbf{r}_3, \\ \rho_2 &= \mathbf{r}_2 - \mathbf{r}_3, \\ \mathbf{R} &= \frac{m_1\mathbf{r}_1 + m_2\mathbf{r}_2 + m_3\mathbf{r}_3}{m_1 + m_2 + m_3}. \end{aligned} \quad (4)$$

In solving Schrödinger's equation, we apply differential operators to the wave function  $\Psi$ . These differential operators contain partial derivatives which are coordinate specific. Thus, the wave function must depend on these same coordinates; and so, any change in the coordinate system being

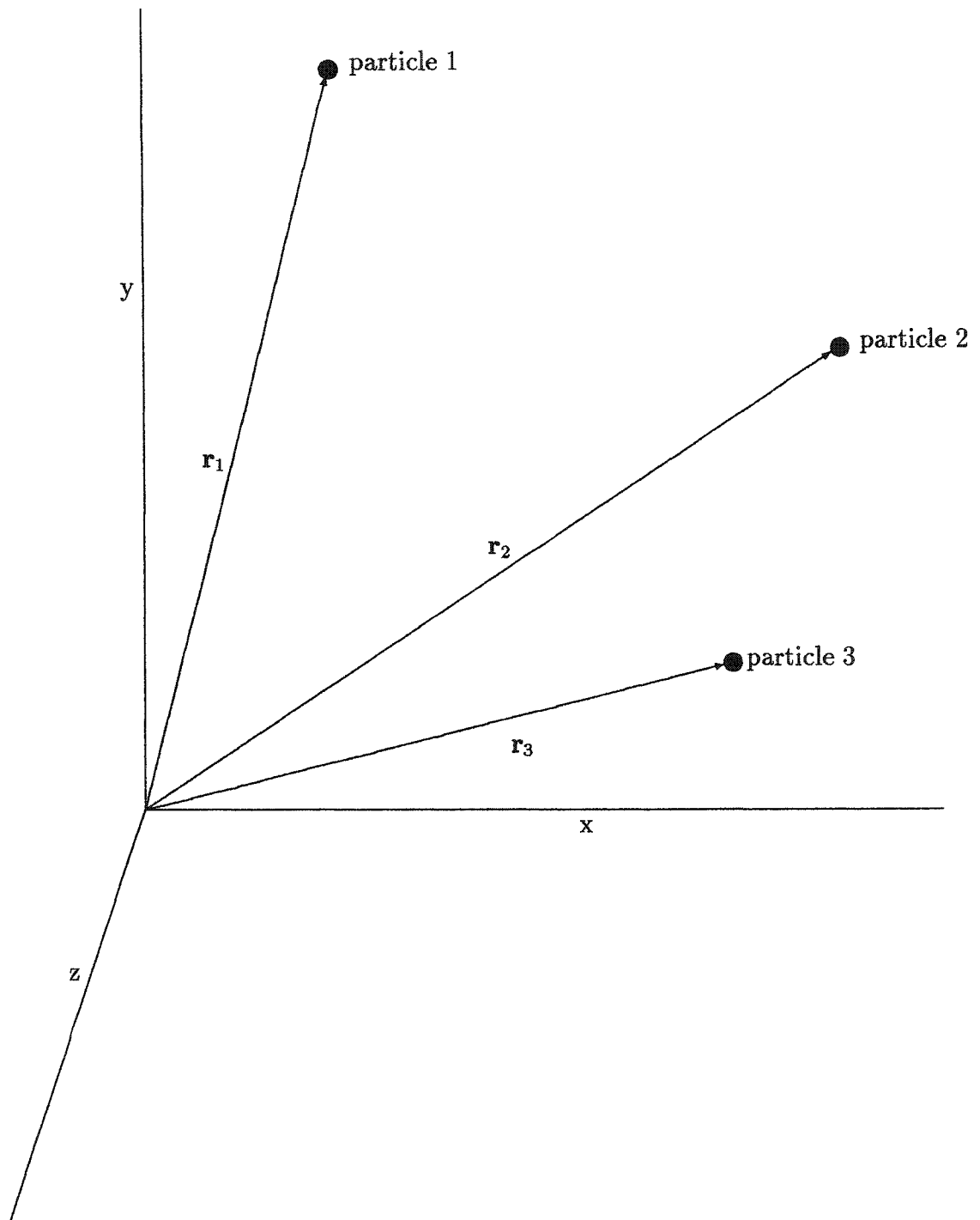


Figure 1: Fixed-origin coordinate system.

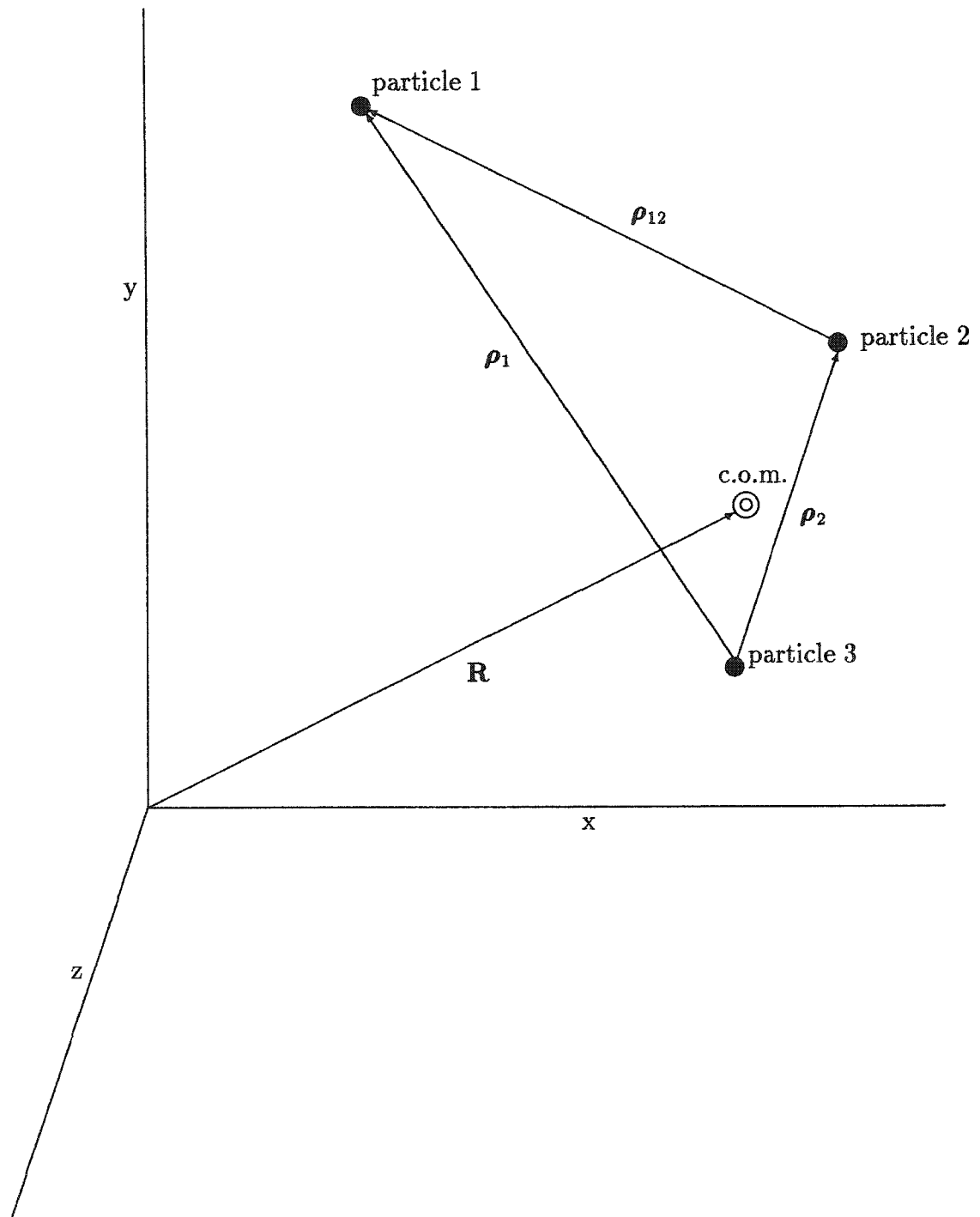


Figure 2: Internal and centre-of-mass coordinate system.

used will result in a change in the form of the wave function and a change in the form of the differential operators:

$$\begin{aligned}\Psi(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3) &\rightarrow \Psi(\boldsymbol{\rho}_1, \boldsymbol{\rho}_2, \mathbf{R}), \\ \nabla_r &\rightarrow \nabla_\rho.\end{aligned}\quad (5)$$

In order to find the new differential operators we simply apply the chain rule; since

$$\nabla_i = \mathbf{i} \frac{\partial}{\partial x_i} + \mathbf{j} \frac{\partial}{\partial y_i} + \mathbf{k} \frac{\partial}{\partial z_i} = \left( \frac{\partial}{\partial x_i}, \frac{\partial}{\partial y_i}, \frac{\partial}{\partial z_i} \right) \quad (6)$$

and

$$\begin{aligned}\frac{\partial}{\partial x_i} &= \frac{\partial \rho_{1x}}{\partial x_i} \frac{\partial}{\partial \rho_{1x}} + \frac{\partial \rho_{2x}}{\partial x_i} \frac{\partial}{\partial \rho_{2x}} + \frac{\partial R_x}{\partial x_i} \frac{\partial}{\partial R_x}, \\ \frac{\partial}{\partial y_i} &= \frac{\partial \rho_{1y}}{\partial y_i} \frac{\partial}{\partial \rho_{1y}} + \frac{\partial \rho_{2y}}{\partial y_i} \frac{\partial}{\partial \rho_{2y}} + \frac{\partial R_y}{\partial y_i} \frac{\partial}{\partial R_y}, \\ \frac{\partial}{\partial z_i} &= \frac{\partial \rho_{1z}}{\partial z_i} \frac{\partial}{\partial \rho_{1z}} + \frac{\partial \rho_{2z}}{\partial z_i} \frac{\partial}{\partial \rho_{2z}} + \frac{\partial R_z}{\partial z_i} \frac{\partial}{\partial R_z},\end{aligned}\quad (7)$$

with  $\mathbf{i}$ ,  $\mathbf{j}$ , and  $\mathbf{k}$  the Cartesian unit vectors, we may determine the required operators in the new coordinates. Letting  $i = 1$  in Eqs. (6) and (7), we have

$$\begin{aligned}\nabla_1 &= \left( \frac{\partial}{\partial x_1}, \frac{\partial}{\partial y_1}, \frac{\partial}{\partial z_1} \right) \\ &= \left( \frac{\partial}{\partial \rho_{1x}}, \frac{\partial}{\partial \rho_{1y}}, \frac{\partial}{\partial \rho_{1z}} \right) \\ &\quad + \left( \frac{m_1}{M} \frac{\partial}{\partial R_x}, \frac{m_1}{M} \frac{\partial}{\partial R_y}, \frac{m_1}{M} \frac{\partial}{\partial R_z} \right),\end{aligned}\quad (8)$$

where  $M = m_1 + m_2 + m_3$ ; this is equivalent to writing

$$\nabla_1 = \nabla_{\rho_1} + \frac{m_1}{M} \nabla_R, \quad (9)$$

where

$$\nabla_{\rho_1} = \mathbf{i} \frac{\partial}{\partial \rho_{1x}} + \mathbf{j} \frac{\partial}{\partial \rho_{1y}} + \mathbf{k} \frac{\partial}{\partial \rho_{1z}} \quad (10)$$

and

$$\nabla_R = \mathbf{i} \frac{\partial}{\partial R_x} + \mathbf{j} \frac{\partial}{\partial R_y} + \mathbf{k} \frac{\partial}{\partial R_z}. \quad (11)$$

The symmetry between the labels 1 and 2 in both coordinate systems allows one to immediately write down

$$\nabla_2 = \nabla_{\rho_2} + \frac{m_2}{M} \nabla_R, \quad (12)$$

where the form for  $\nabla_{\rho_2}$  is given by Eq. (10) with  $1 \rightarrow 2$ .

When  $i = 3$  the form of the operator is slightly more complicated, since  $\mathbf{r}_3$  is our new coordinate origin:

$$\begin{aligned}\nabla_3 &= \left( \frac{\partial}{\partial x_3}, \frac{\partial}{\partial y_3}, \frac{\partial}{\partial z_3} \right) \\ &= - \left( \frac{\partial}{\partial \rho_{1x}}, \frac{\partial}{\partial \rho_{1y}}, \frac{\partial}{\partial \rho_{1z}} \right) - \left( \frac{\partial}{\partial \rho_{2x}}, \frac{\partial}{\partial \rho_{2y}}, \frac{\partial}{\partial \rho_{2z}} \right) \\ &\quad + \left( \frac{m_3}{M} \frac{\partial}{\partial R_x}, \frac{m_3}{M} \frac{\partial}{\partial R_y}, \frac{m_3}{M} \frac{\partial}{\partial R_z} \right).\end{aligned}\tag{13}$$

Equation (13) also has an equivalent vector form:

$$\nabla_3 = -\nabla_{\rho_1} - \nabla_{\rho_2} + \frac{m_3}{M} \nabla_R.\tag{14}$$

The Hamiltonian (2), however, contains  $\nabla_i^2$ , so we must square Eqs. (9), (12) and (14). These operators may be determined, in a straightforward manner, to be:

$$\nabla_1^2 = \left\{ \nabla_{\rho_1} + \frac{m_1}{M} \nabla_R \right\} \cdot \left\{ \nabla_{\rho_1} + \frac{m_1}{M} \nabla_R \right\}\tag{15}$$

$$= \nabla_{\rho_1}^2 + 2 \frac{m_1}{M} \nabla_{\rho_1} \cdot \nabla_R + \left( \frac{m_1}{M} \right)^2 \nabla_R^2,$$

$$\nabla_2^2 = \left\{ \nabla_{\rho_2} + \frac{m_2}{M} \nabla_R \right\} \cdot \left\{ \nabla_{\rho_2} + \frac{m_2}{M} \nabla_R \right\}\tag{16}$$

$$= \nabla_{\rho_2}^2 + 2 \frac{m_2}{M} \nabla_{\rho_2} \cdot \nabla_R + \left( \frac{m_2}{M} \right)^2 \nabla_R^2,$$

and

$$\nabla_3^2 = \left\{ -\nabla_{\rho_1} - \nabla_{\rho_2} + \frac{m_3}{M} \nabla_R \right\} \cdot \left\{ -\nabla_{\rho_1} - \nabla_{\rho_2} + \frac{m_3}{M} \nabla_R \right\}\tag{17}$$

$$= \nabla_{\rho_1}^2 + \nabla_{\rho_2}^2 + \left( \frac{m_3}{M} \right)^2 \nabla_R^2 + 2 \nabla_{\rho_1} \cdot \nabla_{\rho_2}$$

$$- 2 \frac{m_3}{M} (\nabla_{\rho_1} + \nabla_{\rho_2}) \cdot \nabla_R.$$

We now substitute Eqs. (15), (16) and (17) back into the expression for  $H$  and simplify the resulting expression:

$$\begin{aligned}H &= -\frac{\hbar^2}{2m_1} \left\{ \nabla_{\rho_1}^2 + 2 \frac{m_1}{M} \nabla_{\rho_1} \cdot \nabla_R + \left( \frac{m_1}{M} \right)^2 \nabla_R^2 \right\} \\ &\quad - \frac{\hbar^2}{2m_2} \left\{ \nabla_{\rho_2}^2 + 2 \frac{m_2}{M} \nabla_{\rho_2} \cdot \nabla_R + \left( \frac{m_2}{M} \right)^2 \nabla_R^2 \right\}\end{aligned}\tag{18}$$



$$\begin{aligned}
& -\frac{\hbar^2}{2m_3} \left\{ \nabla_{\rho_1}^2 + \nabla_{\rho_2}^2 + \left(\frac{m_3}{M}\right)^2 \nabla_R^2 + 2\nabla_{\rho_1} \cdot \nabla_{\rho_2} \right. \\
& \quad \left. - 2\frac{m_3}{M} \nabla_{\rho_1} \cdot \nabla_R - 2\frac{m_3}{M} \nabla_{\rho_2} \cdot \nabla_R \right\} \\
& + \frac{q_1 q_3}{\rho_1} + \frac{q_2 q_3}{\rho_2} + \frac{q_1 q_2}{\rho_{12}} \\
= & -\frac{\hbar^2}{2} \left(\frac{1}{m_1} + \frac{1}{m_3}\right) \nabla_{\rho_1}^2 - \frac{\hbar^2}{2} \left(\frac{1}{m_2} + \frac{1}{m_3}\right) \nabla_{\rho_2}^2 \\
& - \frac{\hbar^2}{M} \nabla_R^2 - \frac{\hbar^2}{m_3} \nabla_{\rho_1} \cdot \nabla_{\rho_2} + \frac{q_1 q_3}{\rho_1} + \frac{q_2 q_3}{\rho_2} + \frac{q_1 q_2}{\rho_{12}}.
\end{aligned}$$

Switching to reduced masses, defined by

$$\frac{1}{\mu_i} = \frac{1}{m_i} + \frac{1}{m_3}, \quad (19)$$

allows us to write

$$H = -\frac{\hbar^2}{2\mu_1} \nabla_{\rho_1}^2 - \frac{\hbar^2}{2\mu_2} \nabla_{\rho_2}^2 - \frac{\hbar^2}{2M} \nabla_R^2 - \frac{\hbar^2}{m_3} \nabla_{\rho_1} \cdot \nabla_{\rho_2} + \frac{q_1 q_3}{\rho_1} + \frac{q_2 q_3}{\rho_2} + \frac{q_1 q_2}{\rho_{12}}. \quad (20)$$

The potential energy terms in the Hamiltonian contain only relative particle distances, thus showing that the atom as a whole experiences no force; and so, its centre-of-mass motion is a constant. Therefore, we may exclude this term from the Hamiltonian and write (more specifically, any coordinate not appearing in the Hamiltonian is an ignorable coordinate<sup>2</sup> [35])

$$H = -\frac{\hbar^2}{2\mu_1} \nabla_{\rho_1}^2 - \frac{\hbar^2}{2\mu_2} \nabla_{\rho_2}^2 - \frac{\hbar^2}{m_3} \nabla_{\rho_1} \cdot \nabla_{\rho_2} + \frac{q_1 q_3}{\rho_1} + \frac{q_2 q_3}{\rho_2} + \frac{q_1 q_2}{\rho_{12}}. \quad (21)$$

The next step is to remove the multiplicative constants by making a scale change which will put  $H$  in  $Z$ -scaled, reduced mass atomic units [15], that is,

$$r_i = \frac{Z_i}{a_1} \rho_i \implies \frac{\partial}{\partial \rho_i} = \frac{Z_i}{a_1} \frac{\partial}{\partial r_i}, \quad (22)$$

<sup>2</sup>In the Lagrangean formulation, if the coordinate  $q_1$  does not appear in  $T$  or  $V$ , and hence in  $H$ , when  $H$  is the total energy, then the momentum conjugate of this coordinate is a constant of the motion, that is,

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_1} - \frac{\partial L}{\partial q_1} = 0$$

implies, if  $L$  has no  $q_1$  dependence,

$$\frac{d}{dt} \frac{\partial L}{\partial \dot{q}_1} = 0 \implies p_i = \frac{\partial L}{\partial \dot{q}_1} = \text{constant} \implies F = \dot{p} = 0.$$

where  $q_i = Ze$ ,

$$a_1 = \frac{\hbar^2}{\mu_1 e^2} = \frac{m_e}{\mu_1} a_0, \quad (23)$$

and  $a_0 = \hbar^2/(m_e e^2)$  is the first Bohr radius.

If, for the atoms considered, we have two identical particles, and they are chosen to have the labels 1 and 2, we have the further simplification  $Z_1 = Z_2 = Z$ . Taking all of this into account, the Hamiltonian is now

$$H = -\frac{\hbar^2 Z^2}{2\mu_1 a_1^2} \nabla_{r_1}^2 - \frac{\hbar^2 Z^2}{2\mu_2 a_1^2} \nabla_{r_2}^2 - \frac{\hbar^2 Z^2}{m_3 a_1^2} \nabla_{r_1} \cdot \nabla_{r_2} + \frac{Z^2 Z_3 e^2}{a_1 r_1} + \frac{Z^2 Z_3 e^2}{a_1 r_2} + \frac{Z^3 e^2}{a_1 r_{12}}. \quad (24)$$

We also note that for the systems we are dealing with  $Z_3 = -Z$  so that  $Z_3 Z^2 = -Z^3$  so that

$$H = -\frac{\hbar^2 Z^2}{2\mu_1 a_1^2} \nabla_{r_1}^2 - \frac{\hbar^2 Z^2}{2\mu_2 a_1^2} \nabla_{r_2}^2 - \frac{\hbar^2 Z^2}{m_3 a_1^2} \nabla_{r_1} \cdot \nabla_{r_2} - \frac{Z^3 e^2}{a_1 r_1} - \frac{Z^3 e^2}{a_1 r_2} + \frac{Z^3 e^2}{a_1 r_{12}}; \quad (25)$$

but

$$\frac{\hbar^2 Z^2}{2\mu_i a_1^2} = \frac{\hbar^2 Z^2}{2\mu_i a_1} \frac{\mu_1 e^2}{\hbar^2} = \frac{1}{2} \frac{\mu_1}{\mu_i} \frac{Z^2 e^2}{a_1}$$

so that

$$\begin{aligned} H &= -\frac{Z^2 e^2}{2a_1} \nabla_{r_1}^2 - \frac{Z^2 \mu_1 e^2}{2\mu_2 a_1} \nabla_{r_2}^2 - \frac{Z^2 \mu_1 e^2}{m_3 a_1} \nabla_{r_1} \cdot \nabla_{r_2} \\ &\quad - \frac{Z^3 e^2}{a_1 r_1} - \frac{Z^3 e^2}{a_1 r_2} + \frac{Z^3 e^2}{a_1 r_{12}}, \\ \frac{H}{Z^2 e^2/a_1} &= -\frac{1}{2} \nabla_{r_1}^2 - \frac{\mu_1}{2\mu_2} \nabla_{r_2}^2 - \frac{\mu_1}{m_3} \nabla_{r_1} \cdot \nabla_{r_2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{Z}{r_{12}}. \end{aligned} \quad (26)$$

In the end we have the dimensionless Hamiltonian

$$\mathcal{H} = -\frac{1}{2} \nabla_{r_1}^2 - \frac{1}{2} \nabla_{r_2}^2 - \frac{\mu}{m_3} \nabla_{r_1} \cdot \nabla_{r_2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{Z}{r_{12}}, \quad (27)$$

where

$$\mathcal{H} = \frac{H}{Z^2 e^2/a_1};$$

and we have used the fact that (particles 1 and 2 being identical implies  $m_1 = m_2 = m$ )

$$\mu_1 = \mu_2 = \mu = \frac{m m_3}{m + m_3}.$$

We have thus transformed Eq. (1) into its equivalent

$$\mathcal{H}\Psi = \mathcal{E}\Psi, \quad (28)$$

where

$$\mathcal{E} = \frac{E_{\text{NR}}}{Z^2 e^2 / a_1}.$$

For ease of comparison with the literature, we express the nonrelativistic energy in atomic units,

$$\frac{E_{\text{NR}}}{e^2 / a_0} = Z^2 \frac{\mu}{m_e} \mathcal{E}$$

or

$$E_{\text{NR}}(\text{a.u.}) = Z^2 \frac{\mu}{m_e} \mathcal{E},$$

where we have used Eq. (23) and noted that  $\frac{e^2}{a_0} = 1 \text{ a.u.}$ .

## 3.2 Variational Principle

### 3.2.1 Stationary States

High precision calculations for the eigenvalues and eigenfunctions of three-body atomic systems often utilize the variational principle. This technique is employed since, for three-body systems, the form of the Hamiltonian<sup>3</sup> includes correlation, and therefore, makes the Schrödinger equation nonseparable.

If  $|\Psi\rangle$  is an eigenfunction of  $H$  with the corresponding energy eigenvalue  $E$ , we may write [39]

$$H|\Psi\rangle = E|\Psi\rangle. \quad (29)$$

Pre-multiplying this equation by  $\langle\Psi|$  we get

$$\begin{aligned} \langle\Psi|H|\Psi\rangle &= \langle\Psi|E|\Psi\rangle \\ &= E\langle\Psi|\Psi\rangle. \end{aligned} \quad (30)$$

Solving the above for the energy eigenvalue  $E$  gives the quotient

$$E = \frac{\langle\Psi|H|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \quad (31)$$

Since the eigenvalues in the discussion above represent stable atomic states, we know that the eigenfunctions of the Hamiltonian are solutions of the Schrödinger variational principle

$$\delta E = 0. \quad (32)$$

### 3.2.2 Matrix Equivalency

In practice, we write a trial wave function in the form

$$|\Psi_{\text{tr}}\rangle = \sum_{i=1}^N a_i |\phi_i\rangle, \quad (33)$$

where the basis set of functions  $\phi_i$  becomes complete only when the summation is carried out over an infinite number of terms. The linear coefficients

---

<sup>3</sup>In the following, we replace the  $\mathcal{H}$  of Eq. (27) with  $H$  in order to stress that the Hamiltonian need not be written in dimensionless form.

$a_i$  are determined by Eq. (32), where we want the resultant energy to be a minimum.

The explicit form of Eq. (32), where the energy  $E$  depends on any given set of linear parameters  $a_i$ , is

$$\delta E = \sum_i \frac{\partial E}{\partial a_i} \delta a_i = 0. \quad (34)$$

If the  $\delta a_i$  are arbitrary, nonzero variations of the linear coefficients then we require that

$$\frac{\partial E}{\partial a_i} = 0 \quad (35)$$

identically for all  $i$ .

Applying this condition to the energy derived from our trial wave function (33) gives us a system of  $N$  homogeneous linear equations [ $k$  has the same range as  $i$  in Eq. (33)]

$$\frac{\partial E_{\text{tr}}}{\partial a_k} = 0, \quad \text{for all } a_k. \quad (36)$$

Using Eq. (33), we may rewrite Eq. (31) as

$$\begin{aligned} E_{\text{tr}} &= \frac{\langle \Psi_{\text{tr}} | H | \Psi_{\text{tr}} \rangle}{\langle \Psi_{\text{tr}} | \Psi_{\text{tr}} \rangle} \\ &= \frac{\sum_{ij} \langle a_i \phi_i | H | a_j \phi_j \rangle}{\sum_{ij} \langle a_i \phi_i | a_j \phi_j \rangle} \\ &= \frac{\sum_{ij} a_i^* a_j \langle \phi_i | H | \phi_j \rangle}{\sum_{ij} a_i^* a_j \langle \phi_i | \phi_j \rangle} \\ &= \frac{\sum_{ij} a_i^* a_j H_{ij}}{\sum_{ij} a_i^* a_j O_{ij}}, \end{aligned} \quad (37)$$

where  $H_{ij} = \langle \phi_i | H | \phi_j \rangle$  and  $O_{ij} = \langle \phi_i | \phi_j \rangle$ . This allows us to derive an explicit expression for the left-hand side of Eq. (36):

$$\begin{aligned} \frac{\partial E_{\text{tr}}}{\partial a_k} &= \frac{(\sum_{ij} a_i^* a_j O_{ij})(\sum_{ij} a_i^* H_{ij} \delta_{jk}) - (\sum_{ij} a_i^* a_j H_{ij})(\sum_{ij} a_i^* O_{ij} \delta_{jk})}{(\sum_{ij} a_i^* a_j O_{ij})^2} \\ &= \frac{\sum_{ij} a_i^* H_{ik}}{\sum_{ij} a_i^* a_j O_{ij}} - \frac{(\sum_{ij} a_i^* a_j H_{ij})(\sum_i a_i^* O_{ik})}{(\sum_{ij} a_i^* a_j O_{ij})^2} \\ &= \frac{\sum_i a_i^* H_{ik} - E_{\text{tr}} \sum_i a_i^* O_{ik}}{\sum_{ij} a_i^* a_j O_{ij}}, \end{aligned} \quad (38)$$

where we have used Eq. (37) in the last line of Eq. (38).

Now we have

$$\begin{aligned}
\frac{\partial E_{\text{tr}}}{\partial a_k} &= 0 \\
\frac{\sum_i a_i^* H_{ik} - E_{\text{tr}} \sum_i a_i^* O_{ik}}{\sum_{ij} a_i^* a_j O_{ij}} &= 0 \\
\sum_i a_i^* H_{ik} - E_{\text{tr}} \sum_i a_i^* O_{ik} &= 0 \\
\sum_i a_i^* (H_{ik} - E_{\text{tr}} O_{ik}) &= 0.
\end{aligned} \tag{39}$$

Taking the complex conjugate of this, and noting that  $H_{ik}^* = H_{ki}$ ,  $O_{ik}^* = O_{ki}$ , and  $E_{\text{tr}}^* = E_{\text{tr}}$ , we have

$$\sum_i a_i (H_{ki} - E_{\text{tr}} O_{ki}) = 0. \tag{40}$$

According to Eq. (36), the above must be true for all  $k = 1, 2, \dots, N$ . Written explicitly, this is

$$\begin{aligned}
a_1 H_{11} + a_2 H_{12} + \dots + a_N H_{1N} &= E_{\text{tr}} (a_1 O_{11} + a_2 O_{12} + \dots + a_N O_{1N}), \\
a_1 H_{21} + a_2 H_{22} + \dots + a_N H_{2N} &= E_{\text{tr}} (a_1 O_{21} + a_2 O_{22} + \dots + a_N O_{2N}), \\
&\vdots \\
a_1 H_{N1} + a_2 H_{N2} + \dots + a_N H_{NN} &= E_{\text{tr}} (a_1 O_{N1} + a_2 O_{N2} + \dots + a_N O_{NN}),
\end{aligned} \tag{41}$$

or, in terms of matrices, this is

$$\begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & \cdots & H_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix} = E_{\text{tr}} \begin{pmatrix} O_{11} & O_{12} & \cdots & O_{1N} \\ O_{21} & O_{22} & \cdots & O_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ O_{N1} & O_{N2} & \cdots & O_{NN} \end{pmatrix} \begin{pmatrix} a_1 \\ a_2 \\ \vdots \\ a_N \end{pmatrix}. \tag{42}$$

Given that  $H$  has a spectrum of eigenvalues, each with a corresponding eigenvector, we write the equivalent, yet more compact, equation

$$\mathbf{H}\mathbf{a} = E_{\text{tr}}\mathbf{O}\mathbf{a}, \tag{43}$$

where the matrix elements of  $\mathbf{H}$  and  $\mathbf{O}$  are the  $H_{ij}$  and  $O_{ij}$  above, and  $\mathbf{a}$  is the matrix of coefficients

$$\begin{pmatrix} a_{11} & a_{12} & \cdots & a_{1N} \\ a_{21} & a_{22} & \cdots & a_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ a_{N1} & a_{N2} & \cdots & a_{NN} \end{pmatrix}. \tag{44}$$

Diagonalizing  $\mathbf{H}$  will yield  $N$  eigenvalues  $E_{\text{tr}}^j$  ( $j = 1, 2, 3, \dots, N$ ). The  $j$ th column vector of  $\mathbf{a}$ , corresponding to the eigenvalue  $E_{\text{tr}}^j$ , represents the optimum values for the coefficients of  $|\Psi_{\text{tr}}^j\rangle$ . Thus, the  $j$ th column vector of  $\mathbf{a}$  represents  $\Psi_{\text{tr}}$  in the chosen basis.

### 3.2.3 Bounded Solution

Even if  $\Psi$  is not an exact eigenfunction of  $H$ , the Schrödinger variational principle is still useful because the corresponding energy eigenvalue of the function  $\Psi$  is an upper bound to the exact energy eigenvalue. To prove this, an arbitrary trial function can always be expanded in terms of the exact eigenfunctions according to

$$\Psi_{\text{tr}} = \sum_i c_i \varphi_i. \quad (45)$$

The  $\varphi_i$  of Eq. (45), by definition, satisfy the Schrödinger equation

$$H|\varphi_i\rangle = E_i|\varphi_i\rangle, \quad (46)$$

where  $E_0, E_1, E_2, \dots$  are the true eigenvalues in increasing order. Equation (45) is possible, in principle, even though the exact  $\varphi_i$  are not known, since the  $\varphi_i$  span the Hilbert space, i.e., the  $\varphi_i$  form a complete set.

Given the above, the overlap integral may be expressed as

$$\begin{aligned} \langle \Psi_{\text{tr}} | \Psi_{\text{tr}} \rangle &= \sum_{ij} \langle c_i \varphi_i | c_j \varphi_j \rangle \\ &= \sum_{ij} c_i^* c_j \langle \varphi_i | \varphi_j \rangle \\ &= \sum_{ij} c_i^* c_j \delta_{ij} \\ &= \sum_i c_i^* c_i \\ &= \sum_i |c_i|^2. \end{aligned} \quad (47)$$

Now, if  $\Psi_{\text{tr}}$  normalizes to unity we have

$$\langle \Psi_{\text{tr}} | \Psi_{\text{tr}} \rangle = 1 \implies \sum_i |c_i|^2 = 1. \quad (48)$$

We also know that, according to Eq. (31), we can write the energy as

$$E_{\text{tr}} = \frac{\langle \Psi_{\text{tr}} | H | \Psi_{\text{tr}} \rangle}{\langle \Psi_{\text{tr}} | \Psi_{\text{tr}} \rangle} = \langle \Psi_{\text{tr}} | H | \Psi_{\text{tr}} \rangle, \quad (49)$$

where we have used the fact that  $\langle \Psi_{\text{tr}} | \Psi_{\text{tr}} \rangle = 1$ . This allows us to express the trial energy  $E_{\text{tr}}$  as

$$\begin{aligned} E_{\text{tr}} &= \langle \Psi_{\text{tr}} | H | \Psi_{\text{tr}} \rangle \\ &= \sum_{ij} \langle c_i \varphi_i | H | c_j \varphi_j \rangle \\ &= \sum_i \{ \langle c_i \varphi_i | H | c_0 \varphi_0 \rangle + \langle c_i \varphi_i | H | c_1 \varphi_1 \rangle + \dots \} \\ &= \sum_i \{ c_i^* c_0 \langle \varphi_i | E_0 | \varphi_0 \rangle + c_i^* c_1 \langle \varphi_i | E_1 | \varphi_1 \rangle + \dots \} \\ &= \sum_i c_i^* \{ c_0 E_0 \langle \varphi_i | \varphi_0 \rangle + c_1 E_1 \langle \varphi_i | \varphi_1 \rangle + \dots \} \\ &= \sum_i c_i^* \{ c_0 E_0 \delta_{i0} + c_1 E_1 \delta_{i1} + \dots \} \\ &= c_0^* c_0 E_0 + c_1^* c_1 E_1 + \dots \\ &= |c_0|^2 E_0 + |c_1|^2 E_1 + \dots \\ &= \{ 1 - |c_1|^2 - |c_2|^2 - \dots \} E_0 + |c_1|^2 E_1 + |c_2|^2 E_2 + \dots \\ &= E_0 + |c_1|^2 (E_1 - E_0) + |c_2|^2 (E_2 - E_0) + \dots, \end{aligned} \quad (50)$$

since, by Eq. (48),

$$|c_0|^2 = 1 - |c_1|^2 - |c_2|^2 - \dots \quad (51)$$

It is obvious from the above that

$$E_{\text{tr}} \geq E_0, \quad (52)$$

since the  $(E_{i \neq 0} - E_0)$  of Eq. (50) are all positive quantities; thus  $E_{\text{tr}}$  provides an upper bound to the true ground state energy.

### 3.2.4 Higher Eigenvalues

The result of the above section can be extended to higher eigenvalues via the matrix interleaving theorem. The theorem states that when an extra column and row are added to a matrix, the  $N$  old eigenvalues lie between the  $N + 1$  new ones. Since the system is bounded from below and the variational



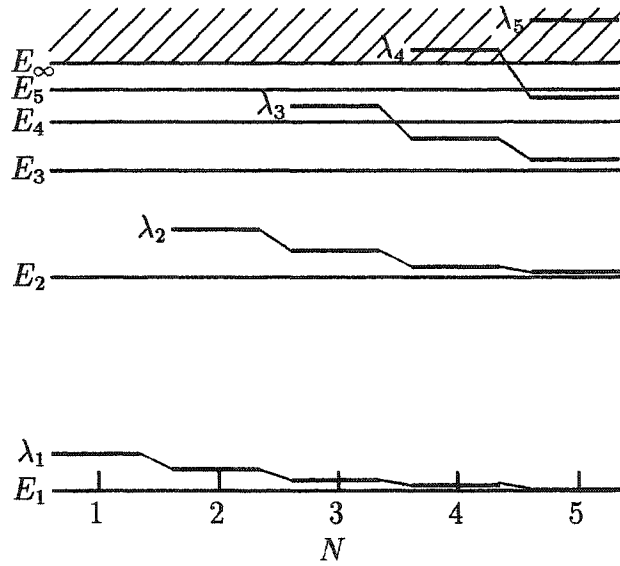


Figure 3: Diagram illustrating the Hylleraas-Undheim-MacDonald Theorem. The  $\lambda_p$ ,  $p = 1, \dots, N$  are the variational eigenvalues for an  $N$ -dimensional basis set, and the  $E_i$  are the exact eigenvalues of  $H$ . The highest  $\lambda_p$  lie in the continuous spectrum of  $H$ .

eigenvalues become the exact eigenvalues in the limit  $N \rightarrow \infty$ , no variational eigenvalue can fall through the corresponding exact eigenvalue. This ensures that the  $N$  variational eigenvalues are upper bounds to the  $N$  true eigenvalues of the system. This is known as the Hylleraas-Undheim-MacDonald [36, 37] theorem in atomic physics. As a result, the  $N$  variational eigenvalues move progressively toward the exact values as  $N$  is increased, as shown in Fig. 3<sup>4</sup>.

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<sup>4</sup>Figure courtesy of Dr. G. W. F. Drake

### 3.3 The Operators in Hylleraas Coordinates

The  $\nabla^2$  in  $\mathcal{H}$  of Eq. (27) are of the form

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \quad (53)$$

where  $x$ ,  $y$ , and  $z$  are simply the Cartesian components of the newly scaled coordinates of Eq. (22), e.g.,

$$\nabla_1^2 = \nabla_{r_1}^2 = \frac{\partial^2}{\partial r_{1x}^2} + \frac{\partial^2}{\partial r_{1y}^2} + \frac{\partial^2}{\partial r_{1z}^2}. \quad (54)$$

These coordinates which we have chosen are the Hylleraas [40, 41] coordinates  $r_1$ ,  $r_2$  and  $r_{12}$ , with

$$\begin{aligned} r_1 &= \sqrt{x_1^2 + y_1^2 + z_1^2}, \\ r_2 &= \sqrt{x_2^2 + y_2^2 + z_2^2}, \\ r_{12} &= r = \sqrt{(x_1 - x_2)^2 + (y_1 - y_2)^2 + (z_1 - z_2)^2}, \end{aligned} \quad (55)$$

for the radial part of the wave function. We now wish to express the partial derivatives explicitly in terms of the Hylleraas coordinates. If we write the wave function as the product

$$\Psi = RY, \quad (56)$$

where  $R$  is a purely radial function and  $Y$  is a purely angular function, we can determine the form of  $\nabla_i^2$  in the new coordinates. Using the product rule

$$\nabla_i \Psi = Y \nabla_i R + R \nabla_i Y = (\nabla_i^R + \nabla_i^Y) \Psi, \quad (57)$$

where operators of the form  $A^R$  and  $A^Y$  are understood to act only on the radial and angular part of the wave function, respectively. In particular, for the radial part and  $i = 1$ , we get

$$\begin{aligned} \nabla_1^R R &= \mathbf{i} \frac{\partial R}{\partial x_1} + \mathbf{j} \frac{\partial R}{\partial y_1} + \mathbf{k} \frac{\partial R}{\partial z_1} \\ &= \mathbf{i} \left\{ \frac{\partial r_1}{\partial x_1} \frac{\partial R}{\partial r_1} + \frac{\partial r_2}{\partial x_1} \frac{\partial R}{\partial r_2} + \frac{\partial r_{12}}{\partial x_1} \frac{\partial R}{\partial r_{12}} \right\} \\ &\quad + \mathbf{j} \left\{ \frac{\partial r_1}{\partial y_1} \frac{\partial R}{\partial r_1} + \frac{\partial r_2}{\partial y_1} \frac{\partial R}{\partial r_2} + \frac{\partial r_{12}}{\partial y_1} \frac{\partial R}{\partial r_{12}} \right\} \end{aligned}$$

$$\begin{aligned}
& + \mathbf{k} \left\{ \frac{\partial r_1}{\partial z_1} \frac{\partial R}{\partial r_1} + \frac{\partial r_2}{\partial z_1} \frac{\partial R}{\partial r_2} + \frac{\partial r_{12}}{\partial z_1} \frac{\partial R}{\partial r_{12}} \right\} \\
= & \mathbf{i} \left\{ \frac{x_1}{r_1} \frac{\partial}{\partial r_1} + \frac{(x_1 - x_2)}{r_{12}} \frac{\partial}{\partial r_{12}} \right\} R \\
& + \mathbf{j} \left\{ \frac{y_1}{r_1} \frac{\partial}{\partial r_1} + \frac{(y_1 - y_2)}{r_{12}} \frac{\partial}{\partial r_{12}} \right\} R \\
& + \mathbf{k} \left\{ \frac{z_1}{r_1} \frac{\partial}{\partial r_1} + \frac{(z_1 - z_2)}{r_{12}} \frac{\partial}{\partial r_{12}} \right\} R \\
= & \{x_1 \mathbf{i} + y_1 \mathbf{j} + z_1 \mathbf{k}\} \frac{1}{r_1} \frac{\partial R}{\partial r_1} \\
& + \{(x_1 - x_2) \mathbf{i} + (y_1 - y_2) \mathbf{j} + (z_1 - z_2) \mathbf{k}\} \frac{1}{r_{12}} \frac{\partial R}{\partial r_{12}} \\
= & \frac{\mathbf{r}_1}{r_1} \frac{\partial R}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial R}{\partial r_{12}}. \tag{58}
\end{aligned}$$

Incorporating the angular part gives us the operator

$$\nabla_1 = \frac{\mathbf{r}_1}{r_1} \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y. \tag{59}$$

One may see from the definitions of  $r_1$ ,  $r_2$  and  $r_{12}$  and  $\nabla_i$  that there is a symmetry between  $\nabla_1$  and  $\nabla_2$ , so that we may immediately write

$$\nabla_2 = \frac{\mathbf{r}_2}{r_2} \frac{\partial}{\partial r_2} + \frac{(\mathbf{r}_2 - \mathbf{r}_1)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_2^Y. \tag{60}$$

Knowing these operators allows us to determine all the operators needed to express  $\mathcal{H}$  in our new coordinates, i.e.,  $\nabla_1^2$ ,  $\nabla_2^2$  and  $\nabla_1 \cdot \nabla_2$ .

We may now use expressions (59) and (60) to define all the operators explicitly appearing in the Hamiltonian  $\mathcal{H}$ . We start with the kinetic energy term  $\nabla_1^2$  (for details see Appendix A.2):

$$\begin{aligned}
\nabla_1^2 \Psi & = \nabla_1 \cdot \nabla_1 \Psi \\
& = \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \cdot \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \Psi \\
& = \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial \Psi}{\partial r_1} \right) + \frac{1}{r_{12}^2} \frac{\partial}{\partial r_{12}} \left( r_{12}^2 \frac{\partial \Psi}{\partial r_{12}} \right) + 2(r_1 - r_2 \cos \theta) \frac{1}{r_{12}} \frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}} \\
& \quad - 2 \frac{(\mathbf{r}_2 \cdot \nabla_1^Y)}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} + (\nabla_1^Y)^2 \Psi.
\end{aligned}$$

The relation  $(\nabla_1^Y)^2 = -l_1^2/r_1^2$  (established in Appendix A.1) gives us the final form for this operator:

$$\nabla_1^2 = \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial}{\partial r_1} \right) + \frac{1}{r_{12}^2} \frac{\partial}{\partial r_{12}} \left( r_{12}^2 \frac{\partial}{\partial r_{12}} \right) \tag{61}$$

$$+ 2(r_1 - r_2 \cos \theta) \frac{1}{r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}} - 2 \frac{(\mathbf{r}_2 \cdot \nabla_1^Y)}{r_{12}} \frac{\partial}{\partial r_{12}} - \frac{l_1^2}{r_1^2}.$$

The operator form for  $\nabla_2^2$  can be found by following a procedure similar to the above, or by the interchange  $1 \longleftrightarrow 2$  in Eq. (61). Explicitly, one would find

$$\begin{aligned} \nabla_2^2 = & \frac{1}{r_2^2} \frac{\partial}{\partial r_2} \left( r_2^2 \frac{\partial}{\partial r_2} \right) + \frac{1}{r_{12}^2} \frac{\partial}{\partial r_{12}} \left( r_{12}^2 \frac{\partial}{\partial r_{12}} \right) \\ & + 2(r_2 - r_1 \cos \theta) \frac{1}{r_{12}} \frac{\partial^2}{\partial r_2 \partial r_{12}} - 2 \frac{(\mathbf{r}_1 \cdot \nabla_2^Y)}{r_{12}} \frac{\partial}{\partial r_{12}} - \frac{l_2^2}{r_2^2}. \end{aligned} \quad (62)$$

The price we pay for transforming the original Hamiltonian into an equivalent two-body form is the introduction of a mass polarization term  $\nabla_1 \cdot \nabla_2$ . If the mass ratio  $\mu/m_3 \ll 1$ , then this term may be treated as a small perturbation to the infinite nuclear mass Hamiltonian. If, on the other hand,  $\mu/m_3 \approx 1$ , the mass polarization term is of a magnitude similar to the kinetic energy terms; and thus, it cannot, to any accuracy, be treated as a small perturbation.

We therefore include this term in the Hamiltonian from the outset. In doing so, we need to determine its operator form in the chosen coordinate system. To do this, we use Eqs. (59) and (60) to write

$$\begin{aligned} \nabla_1 \cdot \nabla_2 \Psi = & \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \\ & \cdot \left\{ \hat{r}_2 \frac{\partial}{\partial r_2} + \frac{(\mathbf{r}_2 - \mathbf{r}_1)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_2^Y \right\} \Psi, \end{aligned} \quad (63)$$

which gives the mass polarization operator to be (see Appendix A.3)

$$\begin{aligned} \nabla_1 \cdot \nabla_2 = & -\frac{1}{r_{12}^2} \frac{\partial}{\partial r_{12}} \left( r_{12}^2 \frac{\partial^2}{\partial r_{12}^2} \right) + \cos \theta \frac{\partial^2}{\partial r_1 \partial r_2} \\ & + \left\{ (\mathbf{r}_1 \cdot \nabla_2^Y) + (\mathbf{r}_2 \cdot \nabla_1^Y) \right\} \frac{1}{r_{12}} \frac{\partial}{\partial r_{12}} \\ & - \left\{ (r_1 - r_2 \cos \theta) \frac{\partial}{\partial r_1} + (r_2 - r_1 \cos \theta) \frac{\partial}{\partial r_2} \right\} \frac{1}{r_{12}} \frac{\partial}{\partial r_{12}} \\ & + (\hat{r}_1 \cdot \nabla_2^Y) \frac{\partial}{\partial r_1} + (\hat{r}_2 \cdot \nabla_1^Y) \frac{\partial}{\partial r_2} + \nabla_1^Y \cdot \nabla_2^Y. \end{aligned} \quad (64)$$

### 3.4 Hamiltonian Matrix Elements.

In order to solve the matrix eigenvalue problem presented by Eq. (43), we need to evaluate the matrix elements corresponding to the Hamiltonian operator:  $H_{pq} = \langle \Phi_p | H | \Phi_q \rangle$ . For the present purpose, we take our trial wave function  $\Psi_{\text{tr}}$  as the expansion

$$\begin{aligned} \Psi_{\text{tr}}(\mathbf{r}_1, \mathbf{r}_2) &= \sum_p c_p \Phi_p \\ &= \sum_p c_p R_p \mathcal{Y}_{l_1 l_2 L}^M(\hat{r}_1, \hat{r}_2), \end{aligned} \quad (65)$$

with the  $\mathcal{Y}_{l_1 l_2 L}^M(\hat{r}_1, \hat{r}_2)$  being vector-coupled products of spherical harmonics,<sup>5</sup> and the  $R_p$  are members of a radial basis set defined, in explicitly correlated Hylleraas coordinates, as

$$R_p = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}, \quad (66)$$

where  $p = \{ijk\}$  represents a distinct combination of powers.

We must now consider how the operator  $\nabla_1^2$  acts on any term in the expansion of the above trial function. Thus, letting the operator of Eq. (61) act upon any  $\Phi_p$  of Eq. (65), we may write

$$\begin{aligned} \nabla_1^2 \Phi_p &= \left\{ \frac{1}{r_1^2} [i(i+1) - l_1(l_1+1)] + \frac{k(k+1)}{r_{12}^2} \right. \\ &\quad - 2 \left[ \frac{\alpha(i+1)}{r_1} + \frac{\gamma(k+1)}{r_{12}} \right] \\ &\quad + \frac{2(r_1 - r_2 \cos \theta)}{r_1 r_{12}^2} [(k - \gamma r_{12})(i - \alpha r_1)] \\ &\quad \left. - \frac{2(\hat{\nabla}_1^{\mathcal{Y}} \cdot \hat{r}_2) r_2}{r_1 r_{12}^2} [k - \gamma r_{12}] + \alpha^2 + \gamma^2 \right\} \Phi_p. \end{aligned} \quad (67)$$

The expression for  $\nabla_2^2$  may be easily obtained by making the following replacements in Eq. (67):  $1 \leftrightarrow 2$ ,  $i \rightarrow j$ , and  $\alpha \rightarrow \beta$ , understanding that  $r_{21} = r_{12}$ .

---

<sup>5</sup>We are here using the coupled representation for the total angular momentum of the system (ion). This representation is connected to the uncoupled representation of products of one-particle angular momentum through coupling, or Clebsch-Gordan, coefficients (see Eq. (71) and Ref. [42]).

The only operator in the Hamiltonian whose action is left to be determined is the mass polarization term, given by

$$-\frac{\mu}{m_3} \nabla_1 \cdot \nabla_2. \quad (68)$$

Letting this operator, given by Eq. (64), act on any  $\Phi_p$ , it can be shown that the matrix elements of the mass polarization operator are

$$\begin{aligned} -\frac{\mu}{m_3} \nabla_1 \cdot \nabla_2 \Phi_p &= -\frac{\mu}{m_3} \left\{ \frac{1}{r_1 r_2} \left[ ij \cos \theta + i(\hat{r}_1 \cdot \hat{\nabla}_2^y) + j(\hat{r}_2 \cdot \hat{\nabla}_1^y) + \hat{\nabla}_1^y \cdot \hat{\nabla}_2^y \right] \right. \\ &\quad + \frac{1}{r_1} \left[ -\beta(i \cos \theta + \hat{r}_2 \cdot \hat{\nabla}_1^y) \right] + \frac{1}{r_2} \left[ -\alpha(j \cos \theta + \hat{r}_1 \cdot \hat{\nabla}_2^y) \right] \\ &\quad + \frac{1}{r_{12}} [\gamma(i + j + 2k + 2)] - \frac{1}{r_{12}^2} [k(k + 1) + jk + ik] \\ &\quad + \frac{r_1}{r_{12}} [\gamma(\beta \cos \theta - \alpha)] + \frac{r_2}{r_{12}} [\gamma(\alpha \cos \theta - \beta)] \\ &\quad + \frac{r_2}{r_{12}^2} [\beta k - \alpha k \cos \theta] + \frac{r_1}{r_{12}^2} [\alpha k - \beta k \cos \theta] \\ &\quad + \frac{r_1}{r_2 r_{12}} \left[ -\gamma(j \cos \theta + \hat{r}_2 \cdot \hat{\nabla}_1^y) \right] \\ &\quad + \frac{r_2}{r_1 r_{12}} \left[ -\gamma(i \cos \theta + \hat{r}_1 \cdot \hat{\nabla}_2^y) \right] \\ &\quad + \frac{r_2}{r_1 r_{12}^2} \left[ k(i \cos \theta + \hat{r}_2 \cdot \hat{\nabla}_1^y) \right] \\ &\quad + \frac{r_1}{r_2 r_{12}^2} \left[ k(j \cos \theta + \hat{r}_1 \cdot \hat{\nabla}_2^y) \right] \\ &\quad \left. + \alpha \beta \cos \theta - \gamma^2 \right\} \Phi_p. \end{aligned} \quad (69)$$

Now that we know the action of all the operators in the Hamiltonian on the various terms in the wave function, we need to evaluate the resulting integrals in order to construct the actual Hamiltonian matrix. To this end, we now investigate the required integrals.

### 3.5 General Integral

The integrals needed for the present calculations have the general form (for details of the following the reader is referred to Refs. [43, 44])

$$\begin{aligned}
I &= \langle \Phi_{p'} | (\text{Op}) | \Phi_p \rangle \\
&= \langle R_{p'} \mathcal{Y}_{l'_1 l'_2 L'}^{M'} | (\text{Op}) | R_p \mathcal{Y}_{l_1 l_2 L}^M \rangle \\
&= \iint d\mathbf{r}_1 d\mathbf{r}_2 R_{p'} \mathcal{Y}_{l'_1 l'_2 L'}^{M'*}(\hat{r}_1, \hat{r}_2) \mathcal{T}_{k_1 k_2 K}^Q \mathcal{Y}_{l_1 l_2 L}^M(\hat{r}_1, \hat{r}_2) R_p,
\end{aligned} \tag{70}$$

where  $\mathcal{Y}_{l'_1 l'_2 L'}^{M'*}(\hat{r}_1, \hat{r}_2)$ ,  $\mathcal{Y}_{l_1 l_2 L}^M(\hat{r}_1, \hat{r}_2)$ , and  $(\text{Op}) = \mathcal{T}_{k_1 k_2 K}^Q(\hat{r}_1, \hat{r}_2)$  are vector-coupled products of spherical harmonics given by

$$\begin{aligned}
\mathcal{Y}_{l_1 l_2 L}^M(\hat{r}_1, \hat{r}_2) &= \sum_{m_1 m_2} \langle l_1 l_2 m_1 m_2 | LM \rangle Y_{l_1}^{m_1}(\hat{r}_1) Y_{l_2}^{m_2}(\hat{r}_2), \\
\mathcal{T}_{k_1 k_2 K}^Q(\hat{r}_1, \hat{r}_2) &= \sum_{q_1 q_2} \langle k_1 k_2 q_1 q_2 | KQ \rangle Y_{k_1}^{q_1}(\hat{r}_1) Y_{k_2}^{q_2}(\hat{r}_2).
\end{aligned} \tag{71}$$

The function  $R_p = R_p(r_1, r_2, r_{12})$  is the correlated radial part of the integral defined by Eq. (66).

Using the fact that the spherical polar coordinates  $\theta_2$  and  $\phi_2$  of  $r_2$  are not independent, but can be expressed in terms of the independent variables  $r_1, r_{12}, \theta_1, \phi_1$ , and  $\chi$  (see Fig. 4)<sup>6</sup> using rotation matrices [45], one can arrive at the basic angular integral algorithm

$$I(l_1 m_1, l_2 m_2; R_{p'} R_p) = 2\pi \delta_{m_1 m_2} \delta_{l_1 l_2} I_l(R_{p'} R_p), \tag{72}$$

where

$$I_l(R' R) = \int_0^\infty r_1 dr_1 \int_0^\infty r_2 dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} r_{12} dr_{12} R_{p'} R_p P_l(\cos \theta_{12}). \tag{73}$$

The radial integral  $I_l(R_{p'} R_p)$  will be considered in the next section. For now, it is important to note that  $\cos \theta_{12}$  is a purely radial function, defined by

$$\cos \theta_{12} = \frac{r_1^2 + r_2^2 - r_{12}^2}{2r_1 r_2}, \tag{74}$$

and  $P_l(\cos \theta_{12})$  is an ordinary Legendre polynomial.

<sup>6</sup>Figure courtesy of Razvan A. Nistor.

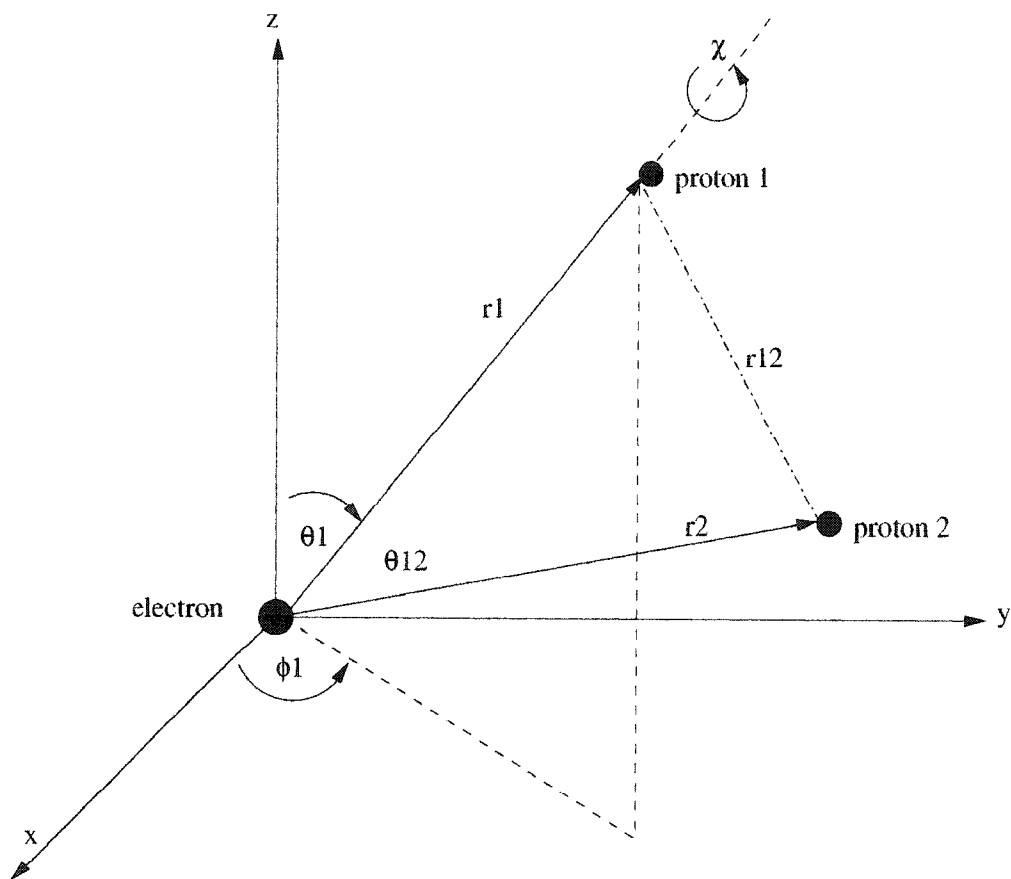


Figure 4: Hylleraas coordinates



The above, in conjunction with standard angular-momentum coupling techniques, allows one to write the general integral in terms of 3- $j$ , 6- $j$ , and 9- $j$  symbols as

$$I = (-)^{L'-M'} \begin{pmatrix} L' & K & L \\ -M' & Q & M \end{pmatrix} \sum_{\lambda_1, \lambda_2, \Lambda} X_{\lambda_1, \lambda_2, \Lambda} D_{\lambda_1, \lambda_2, \Lambda} I_{\Lambda}(R_{p'}, R_p), \quad (75)$$

where  $(a, b, \dots) = (2a+1)(2b+1)\dots$ ,

$$X_{\lambda_1, \lambda_2, \Lambda} = \frac{(-)^{l'_1 + l'_2 + L' + \Lambda}}{8\pi} (\lambda_1, \lambda_2, \Lambda) (l_1, k_1, l'_1, l'_2, L, L', K)^{1/2} \quad (76)$$

$$\times \begin{pmatrix} l_1 & k_1 & \lambda_1 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_1 & \lambda_1 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & k_2 & \lambda_2 \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l'_2 & \lambda_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix},$$

and

$$D_{\lambda_1, \lambda_2, \Lambda} = \begin{Bmatrix} L' & l'_2 & l'_1 \\ \Lambda & \lambda_1 & \lambda_2 \end{Bmatrix} \begin{Bmatrix} l_1 & l_2 & L \\ k_1 & k_2 & K \\ \lambda_1 & \lambda_2 & L' \end{Bmatrix}. \quad (77)$$

The general integral can thus be expressed in the simple form

$$I = \sum_{\Lambda} C_{\Lambda} I_{\Lambda}(R_{p'}, R_p), \quad (78)$$

where

$$C_{\Lambda} = \sum_{\lambda_1, \lambda_2} C_{\lambda_1, \lambda_2, \Lambda} \quad (79)$$

are the angular coefficients, and

$$C_{\lambda_1, \lambda_2, \Lambda} = (-)^{L'-M'} \begin{pmatrix} L' & K & L \\ -M' & Q & M \end{pmatrix} X_{\lambda_1, \lambda_2, \Lambda} D_{\lambda_1, \lambda_2, \Lambda}. \quad (80)$$

For the the case of  $K = 0$  the angular coefficients have the simpler form

$$C_{\Lambda}(1) = \frac{(-1)^{L+\lambda}}{8\pi} (2\Lambda+1) (l_1, l'_1, l_2, l'_2)^{1/2} \begin{pmatrix} l'_1 & l_1 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \quad (81)$$

$$\times \begin{pmatrix} l'_2 & l_2 & \Lambda \\ 0 & 0 & 0 \end{pmatrix} \begin{Bmatrix} L & l_1 & l_2 \\ \Lambda & l'_2 & l'_1 \end{Bmatrix}.$$

### 3.6 Radial Integral

In the present work, the correlated radial part of the wave function has the form

$$R_p(r_1, r_2, r_{12}) = r_1^i r_2^j r_{12}^k e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}. \quad (82)$$

Any integral that we need to evaluate can be reduced to some linear combination of an angular coefficient multiplied by a radial integral of the form

$$I(i, j, k) = \int_0^\infty r_1^{i+1} e^{-\alpha r_1} dr_1 \int_0^\infty r_2^{j+1} e^{-\beta r_2} dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} r_{12}^{k+1} e^{-\gamma r_{12}} dr_{12}. \quad (83)$$

For the specific case of  $i = j = k = -1$ , the integral reduces to

$$I(-1, -1, -1) = \int_0^\infty dr_1 \int_0^\infty dr_2 \int_{|r_1 - r_2|}^{r_1 + r_2} dr_{12} e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}. \quad (84)$$

In order to deal with the absolute value in the limit of this integral we split it into two parts:

$$\begin{aligned} I(-1, -1, -1) &= \int_0^\infty dr_1 \int_{r_1}^\infty dr_2 \int_{r_2 - r_1}^{r_1 + r_2} dr_{12} e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}} \\ &+ \int_0^\infty dr_1 \int_0^{r_1} dr_2 \int_{r_1 - r_2}^{r_1 + r_2} dr_{12} e^{-\alpha r_1 - \beta r_2 - \gamma r_{12}}. \end{aligned} \quad (85)$$

Carrying out the integration we are left with the result

$$I(-1, -1, -1) = \frac{2}{(\alpha + \beta)(\alpha + \gamma)(\beta + \gamma)}. \quad (86)$$

Equation (83) may be used to increase any radial power in the integral by noticing that

$$\begin{aligned} \left(-\frac{\partial}{\partial \alpha}\right) I(i-1, j, k) &= I(i, j, k), \\ \left(-\frac{\partial}{\partial \beta}\right) I(i, j-1, k) &= I(i, j, k), \\ \left(-\frac{\partial}{\partial \gamma}\right) I(i, j, k-1) &= I(i, j, k), \end{aligned} \quad (87)$$

and that all three partial derivatives commute with each other and with the operation of integration. This allows us to generate all higher-power integrals, starting with Eq. (86), by repeated differentiation:

$$I(i, j, k) = (-1)^{i+j+k+3} \frac{\partial^{i+1}}{\partial \alpha^{i+1}} \frac{\partial^{j+1}}{\partial \beta^{j+1}} \frac{\partial^{k+1}}{\partial \gamma^{k+1}} \left[ \frac{2}{(\alpha + \beta)(\alpha + \gamma)(\beta + \gamma)} \right]. \quad (88)$$

Using Leibnitz's notation [46] we write

$$D_\alpha^p \equiv \frac{\partial^{i+1}}{\partial \alpha^{i+1}}, \quad D_\beta^m \equiv \frac{\partial^{j+1}}{\partial \beta^{j+1}}, \quad D_\gamma^n \equiv \frac{\partial^{k+1}}{\partial \gamma^{k+1}}, \quad (89)$$

where  $p = i + 1$ ,  $m = j + 1$ ,  $n = k + 1$ . This implies that

$$D_\alpha^p D_\beta^m D_\gamma^n (uv) = D_\alpha^p D_\beta^m (u'v') = D_\alpha^p (u''v'') = \frac{I(i, j, k)}{(-1)^{p+m+n}}, \quad (90)$$

where

$$\begin{aligned} u &= \frac{1}{(\alpha + \beta)(\alpha + \gamma)}, \\ v &= \frac{2}{(\beta + \gamma)}, \\ D^N(uv) &= uD^N v + \binom{N}{1} (Du)(D^{N-1}v) \\ &\quad + \binom{N}{2} (D^2u)(D^{N-2}v) + \dots + vD^N u, \end{aligned} \quad (91)$$

and  $\binom{N}{1}, \binom{N}{2}, \dots$  are the binomial coefficients.

Performing the required differentiation, we get

$$\begin{aligned} D_\alpha^p (u''v'') &= \sum_{a=0}^p \sum_{b=0}^m \sum_{c=0}^n 2(-1)^{p+m+n} \binom{p}{a} \binom{m}{b} \binom{n}{c} \\ &\quad \times \frac{(a+b)!(c+p-a)!(n+m-b-c)!}{(\alpha+\beta)^{a+b+1}(\alpha+\gamma)^{c+p-a+1}(\beta+\gamma)^{n+m-b-c+1}} \\ &= \sum_{a=0}^p \sum_{b=0}^m \sum_{c=0}^n \frac{2(-1)^{p+m+n} p! m! n!}{a! b! c! (p-a)! (m-b)! (n-c)!} \\ &\quad \times \frac{(a+b)!(c+p-a)!(n+m-b-c)!}{(\alpha+\beta)^{a+b+1}(\alpha+\gamma)^{c+p-a+1}(\beta+\gamma)^{n+m-b-c+1}}. \end{aligned} \quad (92)$$

So now the general radial integral is

$$\begin{aligned} I(p-1, m-1, n-1) &= (-1)^{p+m+n} D_\alpha^p (u''v'') \\ &= \sum_{a=0}^p \sum_{b=0}^m \sum_{c=0}^n \frac{2 p! m! n!}{a! b! c! (p-a)! (m-b)! (n-c)!} \\ &\quad \times \frac{(a+b)!(c+p-a)!(n+m-b-c)!}{(\alpha+\beta)^{a+b+1}(\alpha+\gamma)^{c+p-a+1}(\beta+\gamma)^{n+m-b-c+1}}, \end{aligned} \quad (93)$$

since the factor  $(-1)^{2(p+m+n)} = +1$  for all integer  $p, m, n$ .

It is possible to write this expression in a more compact form if we extract all terms that depend explicitly upon  $a$ . Upon doing so, we may

write

$$I(p-1, m-1, n-1) = \sum_{b=0}^m \sum_{c=0}^n \frac{2p! m! n! (n+m-b-c)!}{b! c! (m-b)! (n-c)!} \quad (94)$$

$$\times \frac{T(b, c, p)}{(\alpha + \beta)^{b+1} (\alpha + \gamma)^{c+p+1} (\beta + \gamma)^{n+m-b-c+1}},$$

where

$$T(b, c, p) = \sum_{a=0}^p \frac{(a+b)! (c+p-a)!}{a! (p-a)!} \left( \frac{\alpha + \gamma}{\alpha + \beta} \right)^a. \quad (95)$$

It is useful, for computational purposes, to note two special cases of this three-dimensional array:

$$T(0, 0, p) = \sum_{a=0}^p \left( \frac{\alpha + \gamma}{\alpha + \beta} \right)^a \quad (96)$$

and

$$T(b, c, 0) = b! c!. \quad (97)$$

## 4 Method of Solution

### 4.1 Solution of the Eigenvalue Problem

To obtain energies for our system we must solve the eigenvalue problem

$$\mathbf{H}\mathbf{a} = E\mathbf{O}\mathbf{a}, \quad (98)$$

where  $H_{pq} = \langle \Phi_p | H | \Phi_q \rangle$ ,  $O_{pq} = \langle \Phi_p | \Phi_q \rangle$ ,  $\Phi$  is that of Eq. (65),  $p, q$  denote distinct combinations of powers  $\{i, j, k\}$  and  $\mathbf{a}$  is a column vector of linear coefficients. There are many ways of solving the above problem; but since we are primarily interested in just the single eigenvalue of the Hamiltonian for the state being optimized, we may utilize what is known as the power method [47].

### 4.2 The Power Method

If  $\mathbf{H}$  is a diagonalizable,  $n \times n$  matrix with eigenvalues  $\lambda_1, \lambda_2, \dots, \lambda_n$  corresponding to the eigenvectors  $\Psi^{(1)}, \Psi^{(2)}, \dots, \Psi^{(n)}$  with ordering  $|\lambda_1| \leq |\lambda_2| \leq \dots < |\lambda_n|$  (i.e.,  $\mathbf{H}$  has a largest eigenvalue  $|\lambda_n| > |\lambda_i|, i \neq n$ ) we may choose an arbitrary starting vector<sup>7</sup>

$$\chi_0 = b_1 \Psi^{(1)} + b_2 \Psi^{(2)} + \dots + b_n \Psi^{(n)}, \quad (99)$$

and then form the sequence

$$\begin{aligned} \mathbf{H}\chi_0 &= b_1 \lambda_1 \Psi^{(1)} + b_2 \lambda_2 \Psi^{(2)} + \dots + b_n \lambda_n \Psi^{(n)} = \chi_1, \\ \mathbf{H}\chi_1 &= b_1 \lambda_1^2 \Psi^{(1)} + b_2 \lambda_2^2 \Psi^{(2)} + \dots + b_n \lambda_n^2 \Psi^{(n)} = \chi_2, \\ &\vdots \\ \mathbf{H}\chi_{k-1} &= b_1 \lambda_1^k \Psi^{(1)} + b_2 \lambda_2^k \Psi^{(2)} + \dots + b_n \lambda_n^k \Psi^{(n)} = \chi_k. \end{aligned} \quad (100)$$

As  $k$  becomes large,  $\chi_k$  becomes the eigenvector of  $\mathbf{H}$  with the largest eigenvalue:

$$\begin{aligned} \chi_k &= b_1 \lambda_1^k \Psi^{(1)} + b_2 \lambda_2^k \Psi^{(2)} + \dots + b_n \lambda_n^k \Psi^{(n)}, \\ \frac{\chi_k}{\lambda_n^k} &= b_1 \left( \frac{\lambda_1}{\lambda_n} \right)^k \Psi^{(1)} + b_2 \left( \frac{\lambda_2}{\lambda_n} \right)^k \Psi^{(2)} + \dots + b_n \Psi^{(n)}; \end{aligned} \quad (101)$$

<sup>7</sup>The following is developed for the nondegenerate case, i.e., the case at hand, but may be extended to include degeneracy [48].

thus, since  $|\lambda_n| > |\lambda_{i \neq n}|$ , and as  $k \rightarrow \infty$ , we are left with

$$\chi_k = a_n \lambda_n^k \Psi^{(n)}, \quad a_n \neq 0. \quad (102)$$

From this we may infer that

$$\chi_{k+1} = a_n \lambda_n^{k+1} \Psi^{(n)} = \lambda_n \chi_k; \quad (103)$$

and since

$$\chi_{k+1} = \mathbf{H} \chi_k \quad (104)$$

we have

$$\mathbf{H} \chi_k = \lambda_n \chi_k. \quad (105)$$

In order for us to be able to pick out any one of the  $n$  eigenvalues of  $\mathbf{H}$ , i.e., to make any one of the eigenvalues dominant, we transform the above in the following way:

$$\begin{aligned} \mathbf{H} \chi &= \lambda_n \mathbf{O} \chi, \\ (\mathbf{H} - \lambda_g \mathbf{O}) \chi &= (\lambda_n - \lambda_g) \mathbf{O} \chi, \\ (\mathbf{H} - \lambda_g \mathbf{O})^{-1} \mathbf{O} \chi &= \frac{1}{(\lambda_n - \lambda_g)} \chi, \\ \mathbf{G} \chi &= \lambda' \chi, \end{aligned} \quad (106)$$

where  $\mathbf{G} = (\mathbf{H} - \lambda_g \mathbf{O})^{-1} \mathbf{O}$  and

$$\lambda' = \frac{1}{(\lambda_n - \lambda_g)}.$$

Choosing  $\lambda_g$  close to any one of the eigenvalues  $\lambda_n$  will make  $\lambda'$  much larger for that  $\lambda_n$  than for any other. We thus form the sequence

$$\begin{aligned} \chi_1 &= \mathbf{G} \chi_0, \\ \chi_2 &= \mathbf{G} \chi_1, \end{aligned} \quad (107)$$

$$\begin{aligned} \chi_3 &= \mathbf{G} \chi_2, \\ &\vdots \end{aligned} \quad (108)$$

until the ratios of the components of two successive  $\chi$ 's stop changing.

The major computational step in the above method is the inversion of a matrix with  $\frac{1}{2}n(n+1)$  elements ( $\mathbf{H}$  is symmetric). This can be replaced by the more efficient process of solving  $n$  equations in  $n$  unknowns as follows:

$$\begin{aligned}\chi_n &= \mathbf{G}\chi_{n-1}, \\ \chi_n &= (\mathbf{H} - \lambda_g \mathbf{O})^{-1} \mathbf{O}\chi_{n-1}, \\ (\mathbf{H} - \lambda_g \mathbf{O})\chi_n &= \mathbf{O}\chi_{n-1}, \\ \mathbf{F}\chi_n &= \mathbf{O}\chi_{n-1},\end{aligned}\tag{109}$$

where  $\mathbf{F} = (\mathbf{H} - \lambda_g \mathbf{O})$  and

$$\lambda_n = \frac{\langle \chi_n | \mathbf{H} | \chi_n \rangle}{\langle \chi_n | \chi_n \rangle}$$

by Eq. (105). This requires us to solve a set of  $n$  inhomogeneous equations. This we do by recourse to the square-root method.

### 4.3 The Square Root Method

In order to solve the set of equations given by the last line of Eq. (109), we use the square-root method [49, 50]. We start by rewriting Eq. (109) as

$$\mathbf{F}\mathbf{x} = \mathbf{y},\tag{110}$$

where  $\mathbf{x} = \chi_n$  and  $\mathbf{y} = \mathbf{O}\chi_{n-1}$ . The first step of this method is carried out by writing

$$\mathbf{F} = \mathbf{S}^T \mathbf{S},\tag{111}$$

where  $\mathbf{S}$  is the upper triangular matrix

$$\begin{pmatrix} s_{11} & s_{12} & \dots & s_{1n} \\ 0 & s_{22} & \dots & s_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \dots & s_{nn} \end{pmatrix}\tag{112}$$

and  $\mathbf{S}^T$  its transpose. The elements of  $\mathbf{S}$ , and consequently  $\mathbf{S}^T$ , are given by

$$\begin{aligned}s_{11} &= \sqrt{f_{11}}, \\ s_{12} &= \frac{f_{12}}{s_{11}}, \\ s_{jj} &= \sqrt{f_{jj} - s_{1j}^2 - s_{2j}^2 - \dots - s_{j-1,j}^2}, \\ s_{jk} &= \frac{f_{jk} - s_{1j}s_{1k} - s_{2j}s_{2k} - \dots - s_{j-1,j}s_{j-1,k}}{s_{jj}},\end{aligned}$$

where the  $f_{jk}$ 's are the known matrix elements of  $\mathbf{F}$ .

Using Eq. (111), we may now write Eq. (110) as

$$\mathbf{S}^T \mathbf{S} \mathbf{x} = \mathbf{y} \quad (113)$$

or, equivalently,

$$\mathbf{S}^T \mathbf{K} = \mathbf{y} \quad \text{and} \quad \mathbf{S} \mathbf{x} = \mathbf{K}. \quad (114)$$

The elements  $k_j$  of  $\mathbf{K}$  may be determined through the use of the following equations:

$$\begin{aligned} k_1 &= \frac{y_1}{s_{11}}, \\ k_2 &= \frac{y_2 - s_{12}k_1}{s_{22}}, \\ k_j &= \frac{y_j - s_{1j}k_1 - s_{2j}k_2 - \dots - s_{j-1,j}k_{j-1}}{s_{jj}}, \end{aligned} \quad (115)$$

where the  $y_j$  are the matrix elements of  $\mathbf{O}\chi_{n-1}$ , which are also known ( $\chi_0$  will be an arbitrary column vector chosen to start the procedure).

We may now use the second equation of (114) to evaluate the sought after components of  $\mathbf{x}$ , since we now know the elements of  $\mathbf{S}$  and  $\mathbf{K}$ . The required equations are

$$\begin{aligned} x_n &= \frac{k_n}{s_{nn}}, \\ x_{n-1} &= \frac{k_{n-1} - s_{n-1,n}x_n}{s_{n-1,n-1}}, \\ x_j &= \frac{k_j - s_{j,j+1}x_{j+1} - s_{j,j+2}x_{j+2} - \dots - s_{jn}x_n}{s_{jj}}, \end{aligned} \quad (116)$$

where we must remember that  $n$  is the dimension of the original matrix  $\mathbf{H}$  whose dominant eigenvector has components  $x_j$ .



## 5 Details of Calculation

### 5.1 The Basis Set

We have utilized a two-sector, or doubled, basis set in all of the calculations presented. These basis sets are a simple modification of those used by Drake [51, 52, 53] and Drake and coworkers [54] to produce essentially exact solutions for helium. This modification came in two stages. The first stage was due to prior work on the positronium negative ion, which lead us to incorporate a  $-\gamma r_{12}$  in the exponential of the usual Hylleraas doubled-basis set [1]. This extra nonlinear parameter allows distance scales to be set along each of the three independent radial coordinates  $r_1$ ,  $r_2$ , and  $r_{12}$ . Such flexibility becomes more and more essential as the atomic mass ratio increases from zero to approximately one.

The second stage of modification is based on the work of Bhatia [20], and Bhatia and Drachman [21], who included an overall factor of  $r_{12}^N e^{-\gamma r_{12}}$  in their basis set. Introducing this factor allows the wave function to localize the proton motion in accordance with the fundamental physical principle underlying the Born-Oppenheimer approximation, i.e., the protons move much more slowly than the electrons since the electron to proton mass ratio is on the order of  $10^{-4}$ . When  $\gamma \approx N/2$  this factor closely approximates a Gaussian function along the internuclear coordinate  $r_{12}$  (see Fig. 5); and so, it allows the vibrational modes of the system to be well represented.

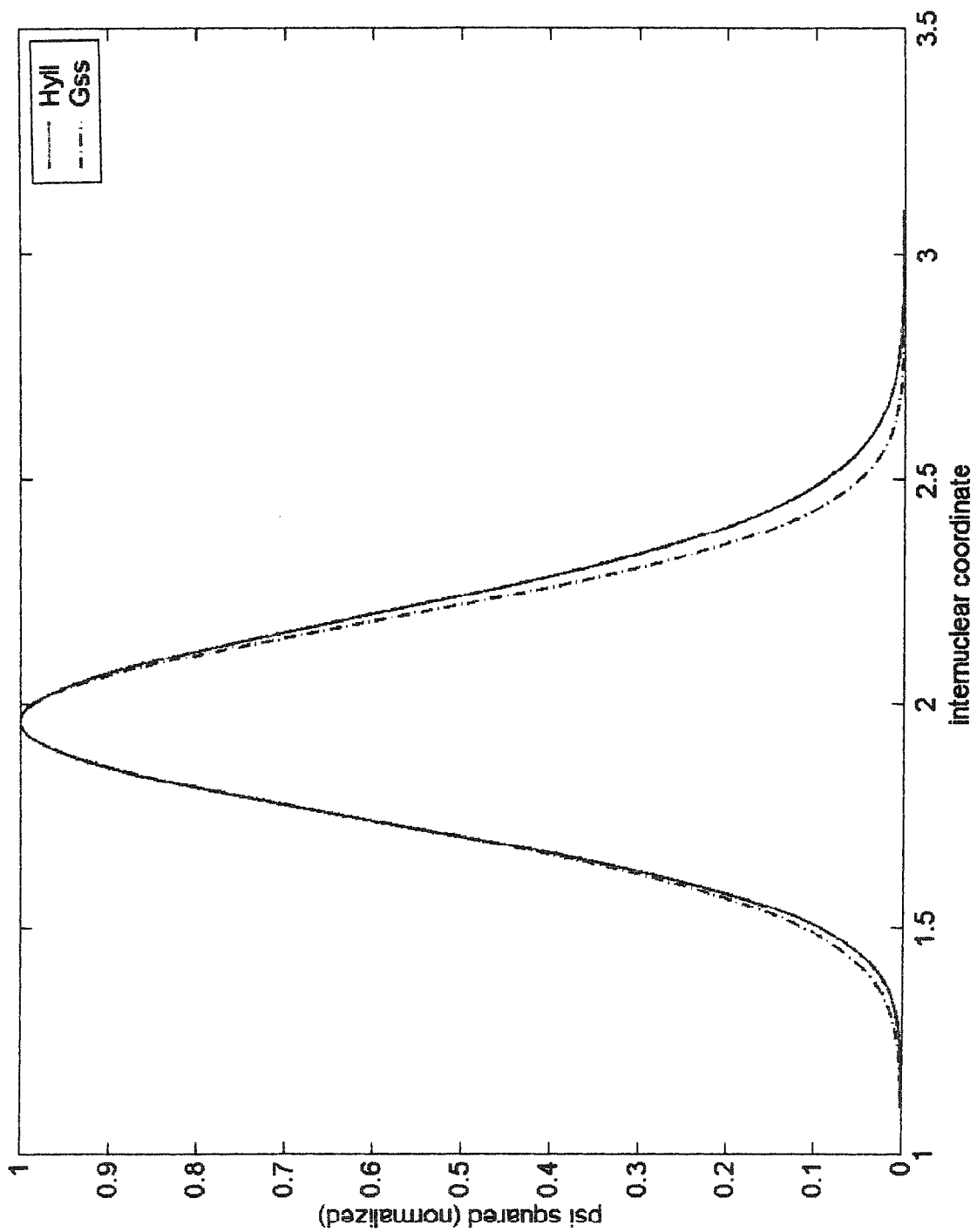
For our modified double basis set, the trial function for  $S$ -states is given by

$$\begin{aligned} \Psi^S(\mathbf{r}_1, \mathbf{r}_2) = & \sum_{p=1}^2 \sum_{i,j=0}^{i+j \leq \Omega_1^{(p)}} \sum_{k=\Omega_{\text{low}}}^{\Omega_{\text{high}}} a_{ijk}^{(p)} r_1^i r_2^j r_{12}^k \\ & \times \exp(-\alpha^{(p)} r_1 - \beta^{(p)} r_2 - \gamma^{(p)} r_{12}) \pm (\text{exchange}), \quad (117) \end{aligned}$$

where the limits for  $k$  are

$$\begin{aligned} \Omega_{\text{low}} &= N_p - \Omega_1^{(p)} + (i + j), \\ \Omega_{\text{high}} &= N_p + \Omega_1^{(p)} - (i + j), \end{aligned}$$

Figure 5: Qualitative comparison of a Gaussian and Hylleraas wave function along the inter-protonic coordinate  $r_{12}$ .



the integers  $N_p > \Omega_1^{(p)}$  are adjustable parameters, and the exchange part is equivalent to the form shown with  $1 \leftrightarrow 2$ , the  $+$  sign for singlet (total spin  $S = 0$ ) states and the  $-$  sign for triplet (total spin  $S = 1$ ) states; and for states with  $L > 0$ ,

$$\Psi^{L>0}(\mathbf{r}_1, \mathbf{r}_2) = \sum_{\text{ang}} \Psi^S(\mathbf{r}_1, \mathbf{r}_2) \mathcal{Y}_{l_1 l_2}^{LM}(\hat{\mathbf{r}}_1, \hat{\mathbf{r}}_2), \quad (118)$$

where  $\sum_{\text{ang}}$  means that all distinct angular couplings are included according to the scheme in Ref. [53].

### 5.1.1 Truncations

Normally, all distinct combinations of powers  $\{i, j, k\}$  would be included in the expansions (117) and (118); however, in order to avoid problems of near linear dependence for  $S$ -states, all terms with  $i > j$  are omitted. In addition, we employed a form of truncation first introduced by Kono and Hattori [55] in which terms with  $i + j + |N_p - k| - |l_1 - l_2| + |j - i| > \Omega_1^{(p)}$  are also avoided. It was also determined that  $\Omega_1^{(1)} = \Omega_1^{(2)}$  gave the best results until larger basis sets ( $> 1100$ ), where problems of near linear dependence started to arise.

### 5.1.2 Choosing $N_1$ and $N_2$

An initial choice of  $N_2 = 35$  was based on the work of Yan *et al.* [34]. We then varied  $N_1$  to find its optimal value. This procedure was then carried out for different values of  $N_2$ . A similar procedure was carried out by first fixing  $N_1$ , and then varying  $N_2$ . Typical results are shown in Table 2. In such a manner it was found that with complete optimization, in general, a lower energy was attained when  $N_1 = N_2$ . This result is reasonable, since both sectors of the basis set must be able to accurately represent the *same* vibrational mode of the system for any given state (see Sect. 5.1).

### 5.1.3 Radial Completeness

The standard Hylleraas-type radial basis was proven complete by Klahn and Bingel [56]. Although at first, the radial basis used in this work excludes lower powers of  $r_{12}$ , these powers reappear as  $\Omega_1$  is increased. Thus, for

Table 2: Variation of ground state energy with  $N_1$  and  $N_2$ .

$N_1$	$N_2$	Energy	$N_1$	$N_2$	Energy
30	35	-0.597 139 062 385 650	36	30	-0.597 139 061 906 769
31	35	-0.597 139 062 608 263	36	31	-0.597 139 062 643 068
32	35	-0.597 139 062 734 106	36	32	-0.597 139 062 943 849
33	35	-0.597 139 062 853 780	36	33	-0.597 139 063 053 430
34	35	-0.597 139 062 963 500	36	34	-0.597 139 063 046 652
35	35	-0.597 139 063 023 229	36	35	-0.597 139 063 067 699
36	35	-0.597 139 063 067 699	36	36	-0.597 139 063 083 416
37	35	-0.597 139 063 054 221	36	37	-0.597 139 063 080 049
38	35	-0.597 139 062 998 248	36	38	-0.597 139 063 069 018
39	35	-0.597 139 062 939 545	36	39	-0.597 139 063 051 702
40	35	-0.597 139 062 885 259	36	40	-0.597 139 063 041 122

any finite  $N_p$ , the expansions (117) and (118) will be complete by the same argument as that for the standard Hylleraas basis set as the number of terms becomes infinite.

## 5.2 Optimization

A complete optimization of the energy  $E$  with respect to all six nonlinear parameters was carried out for each basis set size (see Ref. [53]). This is done by calculating the first derivatives

$$\begin{aligned}\frac{\partial E}{\partial \alpha^{(p)}} &= -2\langle \Psi_{\text{tr}} | H | r_1 \psi(\mathbf{r}_1, \mathbf{r}_2; \alpha^{(p)}) \pm r_2 \psi(\mathbf{r}_2, \mathbf{r}_1; \alpha^{(p)}) \rangle, \\ \frac{\partial E}{\partial \beta^{(p)}} &= -2\langle \Psi_{\text{tr}} | H | r_1 \psi(\mathbf{r}_1, \mathbf{r}_2; \beta^{(p)}) \pm r_2 \psi(\mathbf{r}_2, \mathbf{r}_1; \beta^{(p)}) \rangle, \\ \frac{\partial E}{\partial \gamma^{(p)}} &= -2\langle \Psi_{\text{tr}} | H | r_1 \psi(\mathbf{r}_1, \mathbf{r}_2; \gamma^{(p)}) \pm r_2 \psi(\mathbf{r}_2, \mathbf{r}_1; \gamma^{(p)}) \rangle,\end{aligned}$$

where  $\psi(\mathbf{r}_1, \mathbf{r}_2; \alpha^{(p)})$  denotes only the terms in  $\Psi_{\text{tr}}$  that depend explicitly on  $\alpha^{(p)}$ , and unit norm has been assumed.

The derivatives contain no contribution from an implicit dependence of the energy on the nonlinear parameters through the linear coefficients  $a_{ijk}^{(p)}$ , i.e., from terms of the form

$$\frac{\partial E}{\partial \alpha^{(p)}} = \frac{\partial E}{\partial a_{ijk}^{(p)}} \frac{\partial a_{ijk}^{(p)}}{\partial \alpha^{(p)}} + \dots \quad (119)$$

This is because Eq. (35) ensures that these contributions are zero (at least to

first order), that is, the energy is stable with respect to first order variations in the linear coefficients.

Knowing the first derivatives allows us to estimate the second derivatives by changing the  $\alpha^{(p)}$ 's,  $\beta^{(p)}$ 's, and  $\gamma^{(p)}$ 's in the direction of lower energy and taking differences. We then apply Newton's method to the first derivatives to find the zeros. If the initial choice of nonlinear parameters is good (i.e., close to a minimum), this method converges in a few iterations.

## 6 Results and Discussion

Developing a systematic way of calculating the energy eigenvalues and corresponding eigenfunctions for arbitrary three-body quantum systems has been the main goal of this work. Previous work using doubled-basis sets in Hylleraas coordinates [1, 51, 52, 54] proved that such an approach provided well converged energies, as well as stable and compact wave functions, for helium,  $\text{H}^-$ , and  $\text{Ps}^-$ , where the mass ratio  $\mu/\mathcal{M}$  varies from  $\approx 0.0001$  to 0.5. We now present the results of the variational calculations that were carried out for the nonrelativistic energy eigenvalues for the  $1\ ^1S$ ,  $2\ ^1S$ , and  $2\ ^3P$  states of  $\text{H}_2^+$ , where  $\mu/\mathcal{M} \approx 1$ . A value of 1836.152 701 was used for the proton mass [57], even though an improved value is available [58], in order to allow comparison with other theoretical work. Studies of the convergence patterns for these three states are given in Tables 5, 6, and 7. As these Tables show, the present method of calculation, involving the seven parameters  $\alpha^{(1)}$ ,  $\beta^{(1)}$ ,  $\gamma^{(1)}$ ,  $\alpha^{(2)}$ ,  $\beta^{(2)}$ ,  $\gamma^{(2)}$ , and  $N (= N_1 = N_2)$ , does indeed allow the highly-accurate determination of the energy eigenvalues of a wide range of three-body systems. It must be noted that all calculations were done in quadruple precision (about 32 decimal digits) arithmetic on SHARCnet's *Tiger* cluster of Compaq Alpha ES40 workstations; thus, the need for multiple precision arithmetic is avoided, at least when the present level of accuracy is required.

The ratios given in the last column of Tables 5, 6, and 7 are defined by

$$R(\Omega) = \frac{E(\Omega - 1) - E(\Omega - 2)}{E(\Omega) - E(\Omega - 1)}, \quad (120)$$

where  $\Omega = N + \Omega_1$ , and thus give the values of the ratios of successive differences in the energies. If  $R(\Omega)$  were constant, the extrapolated value of the energy would simply be the series limit of a geometric series. Since this is not the case, we fit the ratios to the form  $a/\Omega^b$  and sum the series of differences to obtain the extrapolated value. The final quoted uncertainty is thus determined from the uncertainty in the parameters  $a$  and  $b$ .

A comparison with other theoretical values for the same states was given in Table 1 of Section 2, and a portion of that data is reproduced in Table 3.

For the three states calculated, our largest basis set gives the lowest upper bound to date. However, although different basis sets and methods have been used, it is satisfying that all the results agree to within their estimated uncertainties.

Table 3: Comparison of calculated energies with the best values found in the literature.

Author	Year	Energy
$1\ ^1S$		
Korobov [26]	2000	-0.597 139 063 123 405 074
Bailey and Frolov [31]	2002	-0.597 139 063 123 405 074 83
Yan <i>et al.</i> [34]	2003	-0.597 139 063 123 405 074 5(4)
This work		-0.597 139 063 123 405 074 834 337 7(21)
$2\ ^1S$		
Grémaud <i>et al.</i> [19]	1998	-0.587 155 679 212(1)
Moss [24, 23]	1999	-0.587 155 679 212 8
Hilico <i>et al.</i> [27]	2000	-0.587 155 679 212 75(1)
This work		-0.587 155 679 212 746 812 212 1(17)
$2\ ^3P$		
Taylor <i>et al.</i> [22]	1999	-0.596 873 738 832 8(5)
Moss [23]	1999	-0.596 873 738 832 8
Yan <i>et al.</i> [34]	2003	-0.596 873 738 832 764 733(1)
This work		-0.596 873 738 832 764 734 958(43)

For a given state,  $N$  is varied until a minimum in the energy is found for a given basis set size. This procedure is carried out for all basis set sizes considered, as shown in Fig. 6. The  $N$  that minimizes the energy for the largest basis set used is taken as the optimum value. It is then fixed at this value for all basis set sizes as  $\Omega_1$  is increased. In this way, it was found that  $N = 39, 38, 37$  gave the minimum energy, and good convergence, for the  $1\ ^1S$ ,  $2\ ^1S$ , and  $2\ ^3P$  states, respectively. In addition, the condition  $\gamma^{(p)} \approx N_p/2$  of Ref. [20] naturally appears in this calculation upon optimization of the energy  $E$  with respect to  $\gamma$ . This is shown explicitly in Table 4, where the values for  $\gamma^{(p)}$  have been taken from Tables 8, 9, and 10. These accompanying large values of the  $\gamma$ 's (compared to the  $\alpha$ 's and  $\beta$ 's), in both sets, seen also in Figs. 8, 10, and 12, are essential to properly account for the vibrational nuclear wave function which is known from the Born-Oppenheimer approximation to be Gaussian-like.

Table 4: Average values of  $\gamma^{(1)}$  and  $\gamma^{(2)}$ .

State	N	N/2	$\gamma_{\text{avg}}^{(1)}$	$\gamma_{\text{avg}}^{(2)}$
1 $^1S$	39	19.5	19.34	19.13
2 $^1S$	38	19.0	18.15	18.32
2 $^3P$	37	18.5	18.48	18.52

The inclusion of two sets of nonlinear parameters provides a detailed description of the physical nature of the problem: one set of  $\alpha$ 's and  $\beta$ 's describes the asymptotic behaviour of the wave function, while the other set describes the inner, short-range behaviour. This partitioning of the wave function is clearly shown for the 1  $^1S$  state in Fig. 7. The optimized  $\alpha^{(2)}$  and  $\beta^{(2)}$  remain fairly constant (asymptotic part) while the  $\alpha^{(1)}$  and  $\beta^{(1)}$  increase steadily with  $\Omega$  (short-range part). This behaviour of the wave function is not as easily seen for the 2  $^1S$  (Fig. 9) and 2  $^3P$  (Fig. 11) states. This may simply be due to multiple minima existing on the energy surface. That these minima do exist can be demonstrated as follows: for the 2  $^1S$  state, the optimized values of  $\alpha^{(1)}$  and  $\beta^{(1)}$  for 1015 terms in the basis set gave an energy of  $-0.587\,155\,679\,212\,746\,812\,191$ , while interchanging these values for  $\alpha^{(1)}$  and  $\beta^{(1)}$  gave a minimum energy of  $-0.587\,155\,679\,212\,746\,812\,147$ . The difference in energy being within the estimated uncertainty clearly shows that more than one minima exists.

The stability of the energy eigenvalues with respect to changes in the nonlinear parameters was also checked. A relative change in  $\alpha$  of

$$\frac{\Delta\alpha}{\alpha} \approx 10^{-2}$$

introduced a relative change in the energy  $E$  of

$$\frac{\Delta E}{E} \approx 10^{-21}.$$

Knowing the value of the derivative of the energy with respect to  $\alpha$  to be on the order of  $10^{-19}$  allows an estimate of the expected change in the energy:

$$(\Delta E)_{\text{exp}} \approx \frac{\partial E}{\partial \alpha} \Delta\alpha \approx 10^{-21}.$$

Thus, the agreement is as it should be; and the stability, as such, verified.



Figure 6: Optimum  $N$  for varying basis set size.

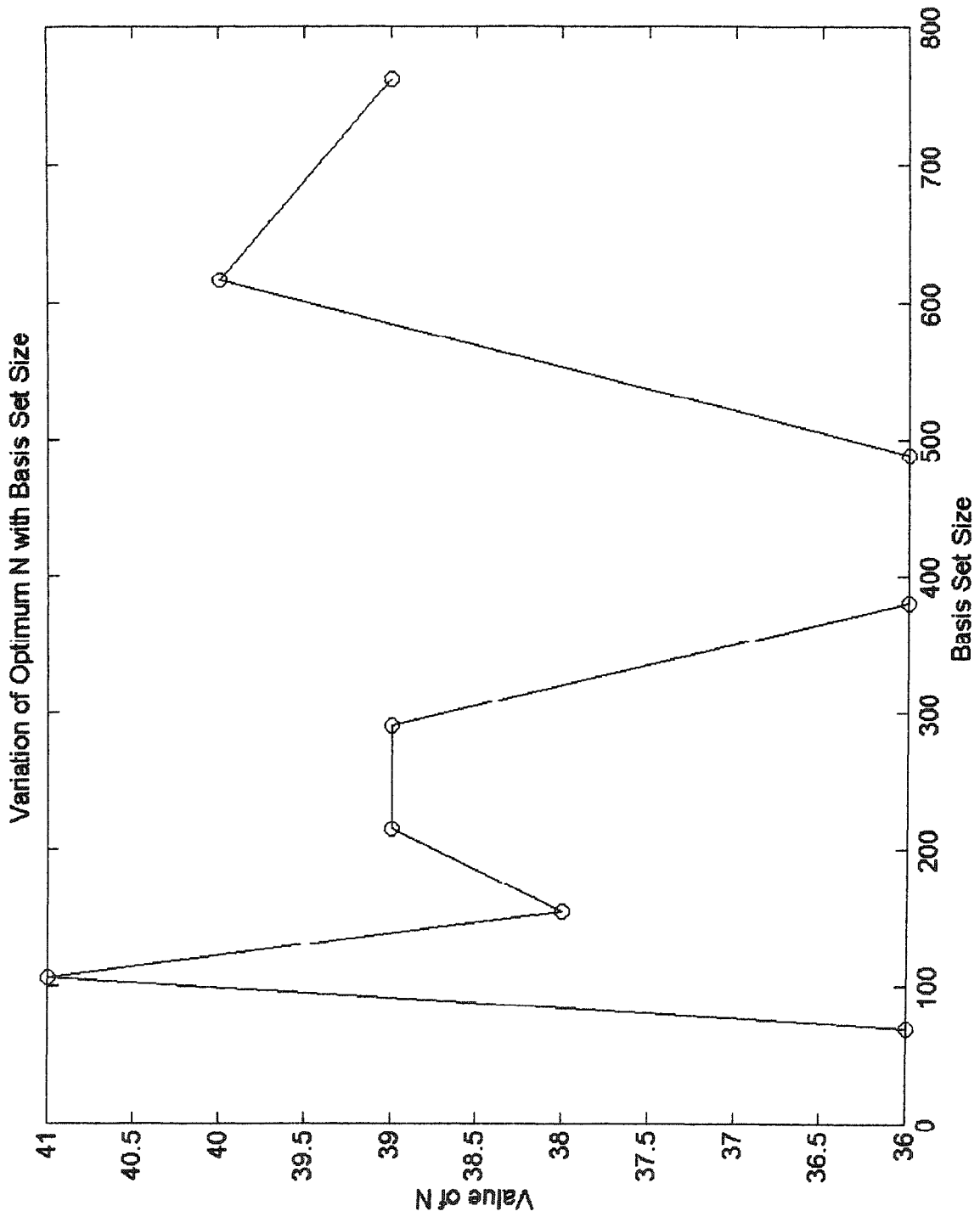


Figure 7: Graph of  $\alpha$ 's and  $\beta$ 's versus  $\Omega$  for the  $1\ ^1S$  state.

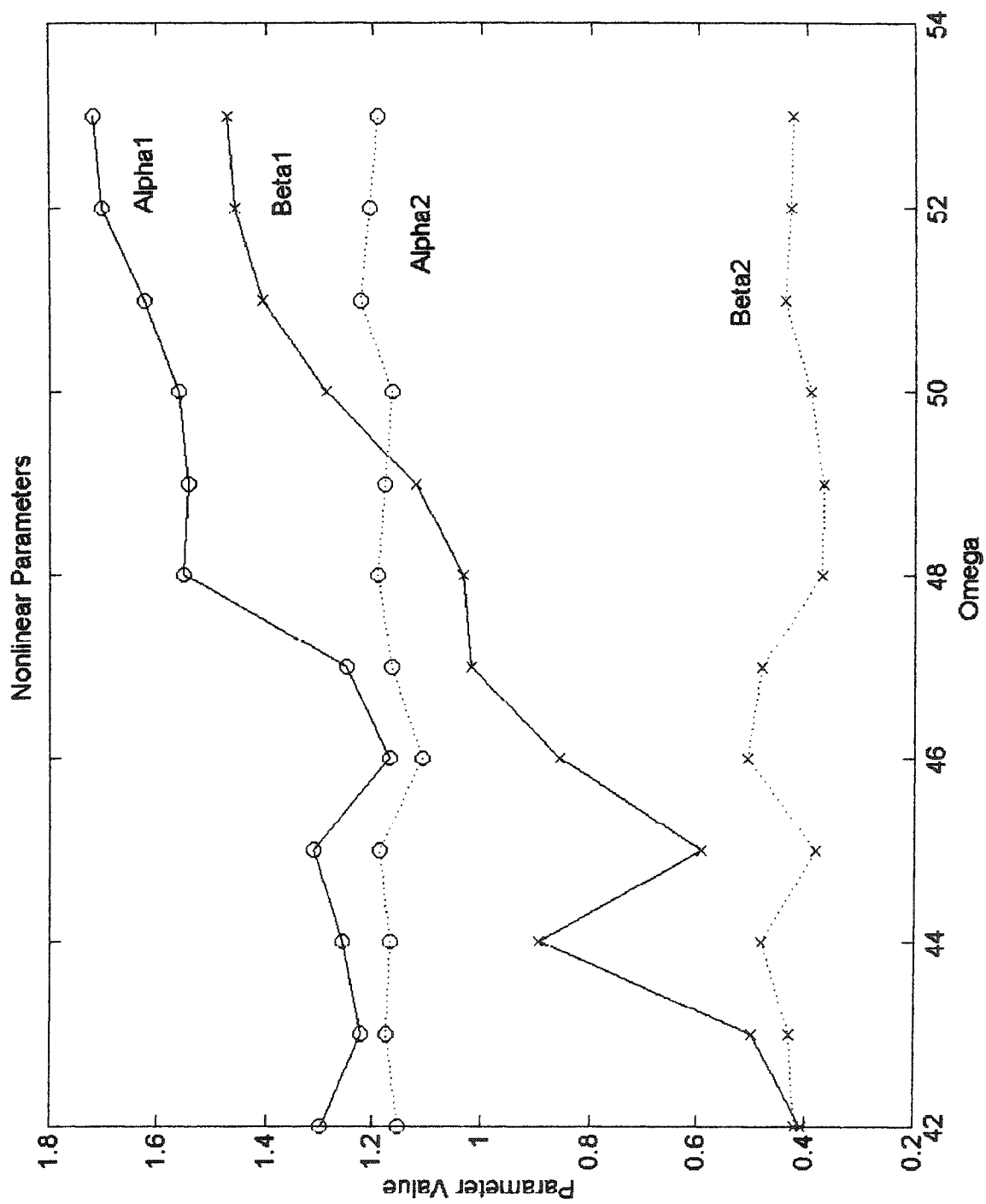


Figure 8: Graph of  $\gamma$ 's versus  $\Omega$  for the  $1^1S$  state.

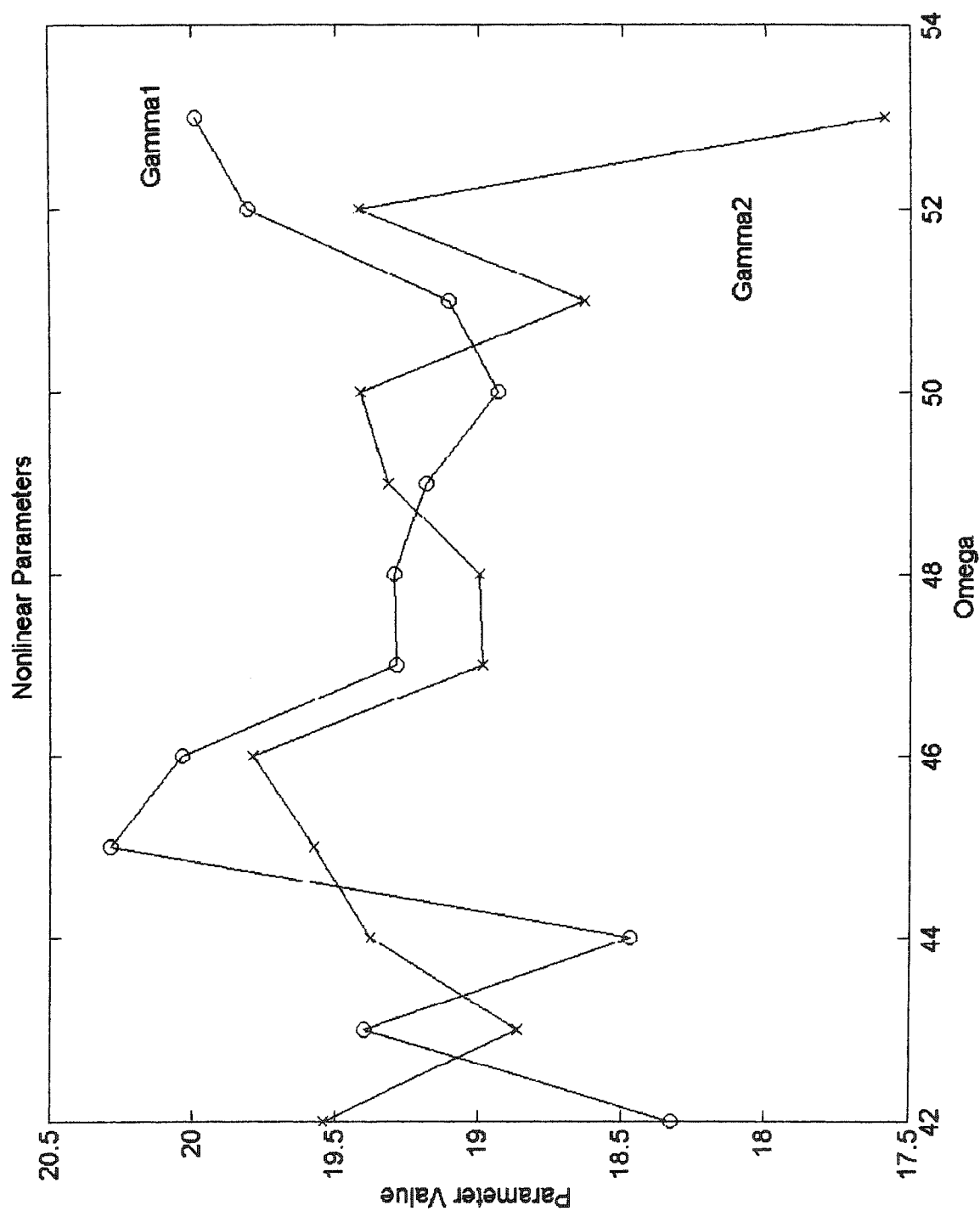


Figure 9: Graph of  $\alpha$ 's and  $\beta$ 's versus  $\Omega$  for the  $2^1S$  state.

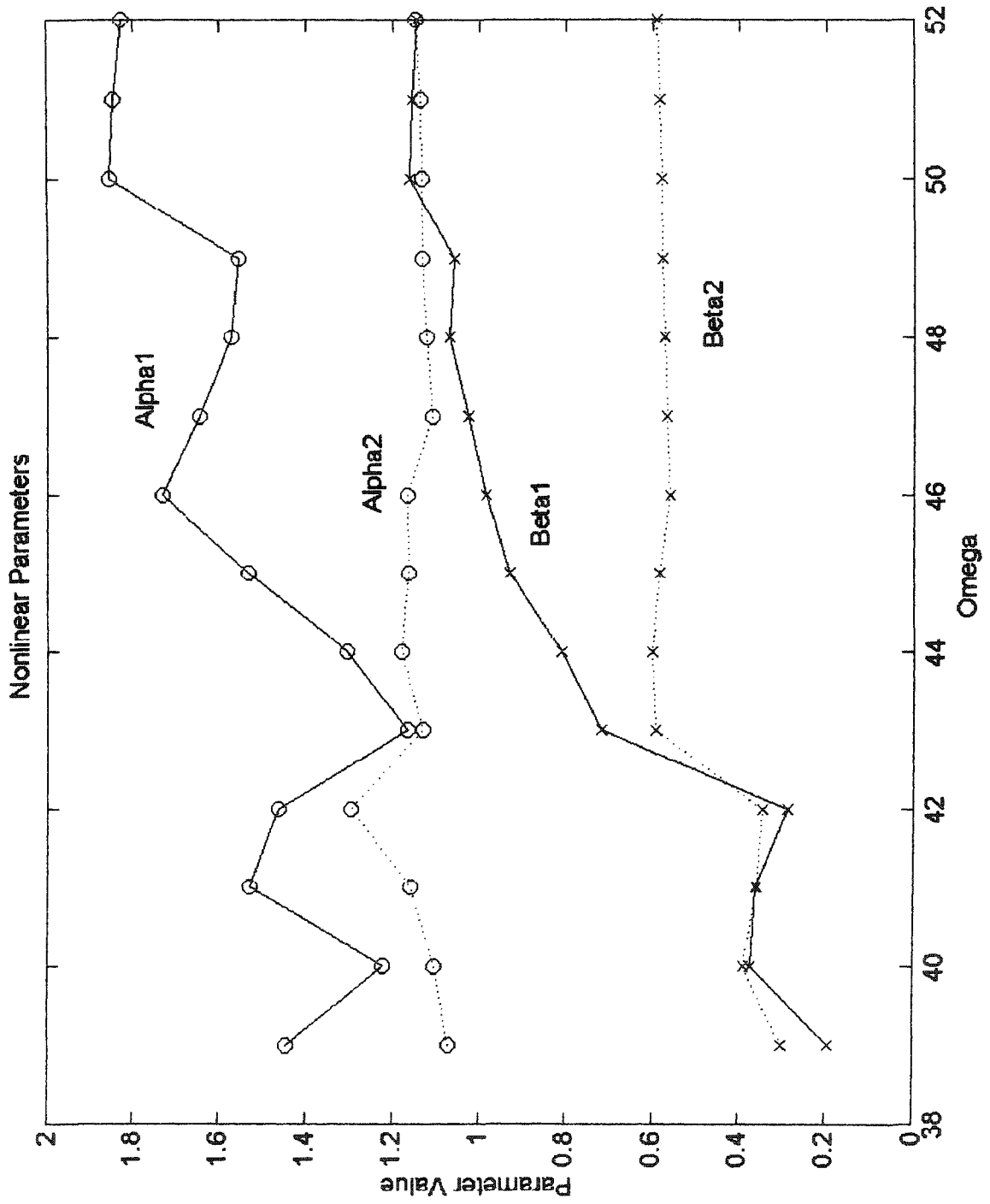


Figure 10: Graph of  $\gamma$ 's versus  $\Omega$  for the  $2^1S$  state.

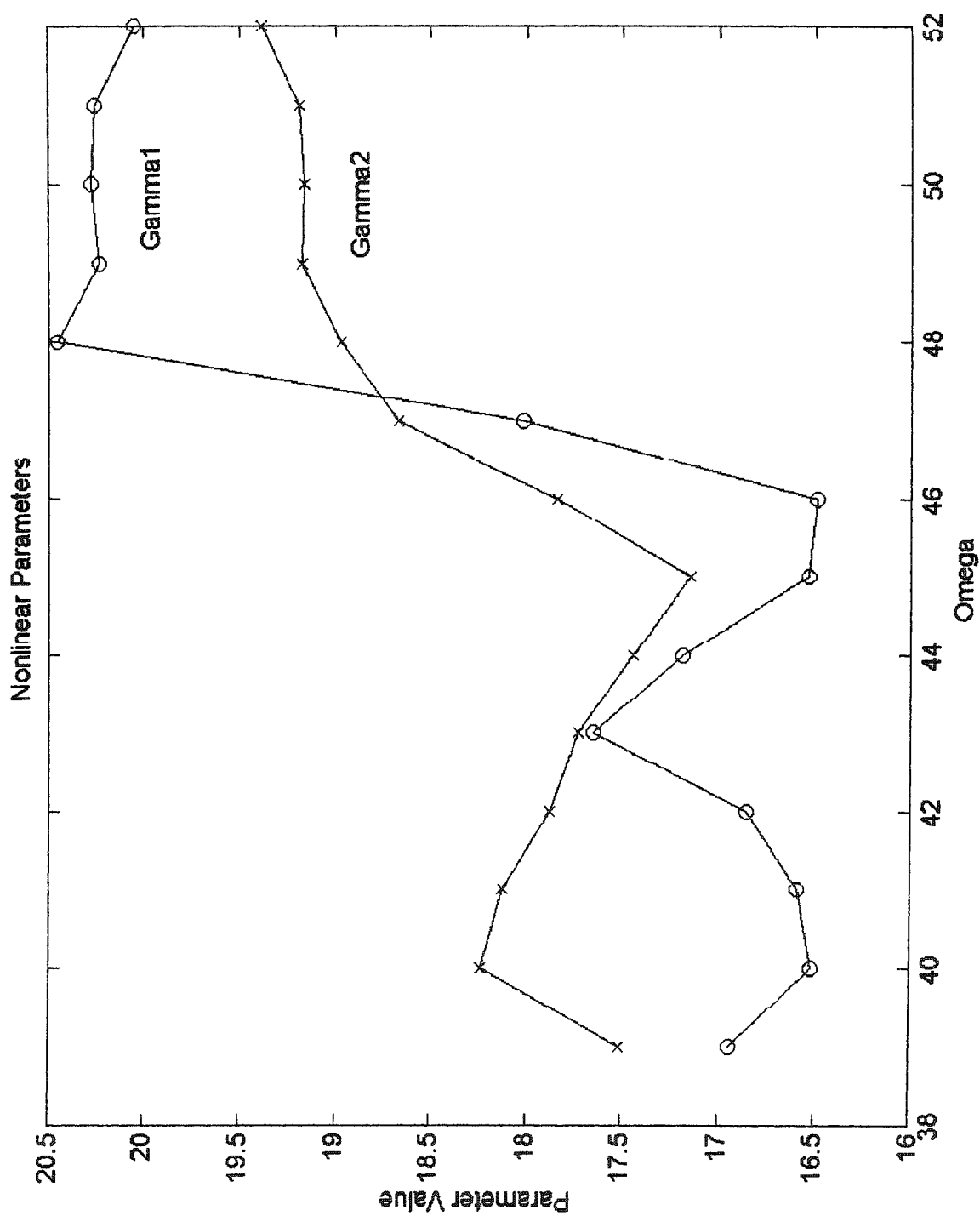


Figure 11: Graph of  $\alpha$ 's and  $\beta$ 's versus  $\Omega$  for the  $2^3P$  state.

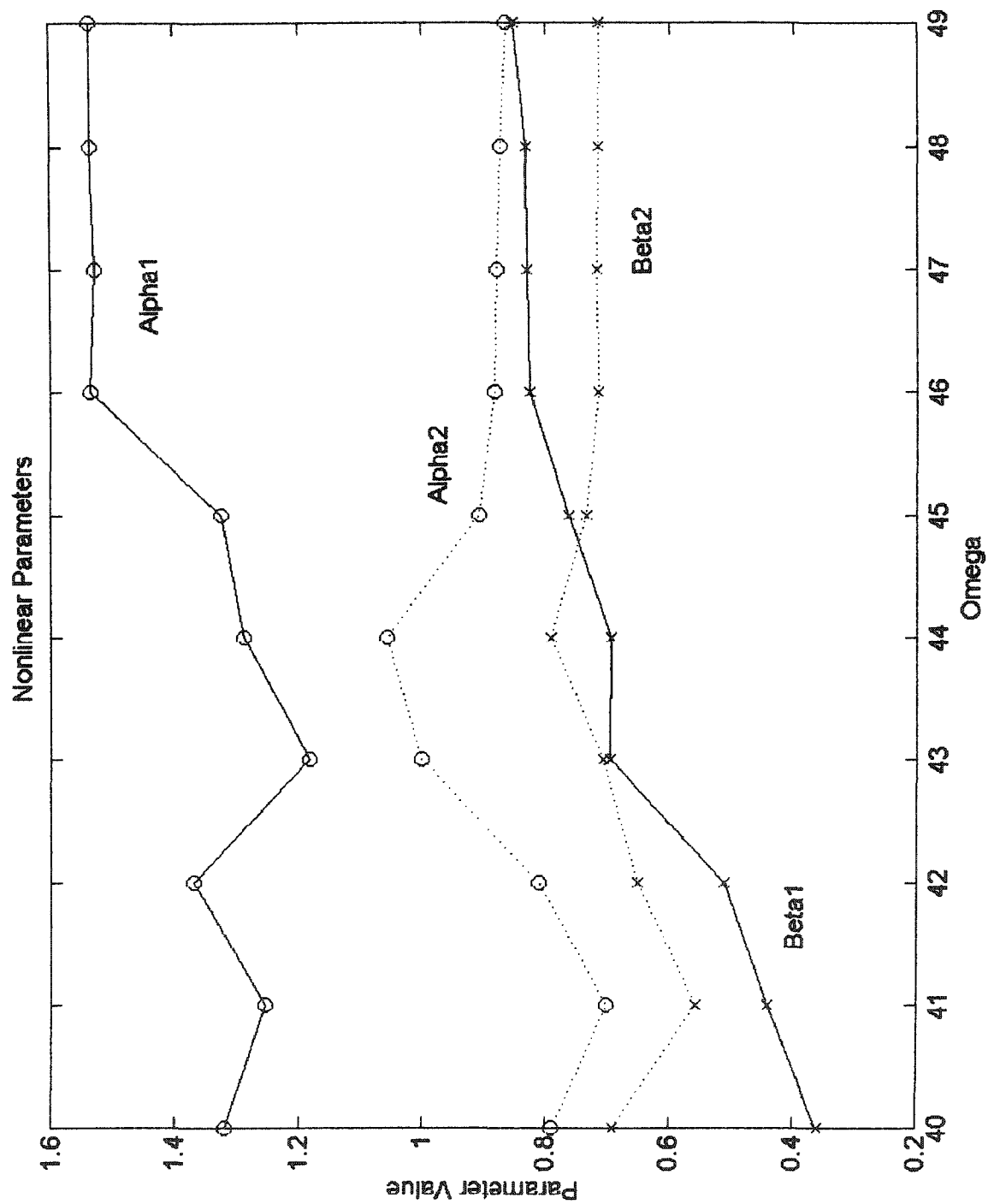


Figure 12: Graph of  $\gamma$ 's versus  $\Omega$  for the  $2^3P$  state.

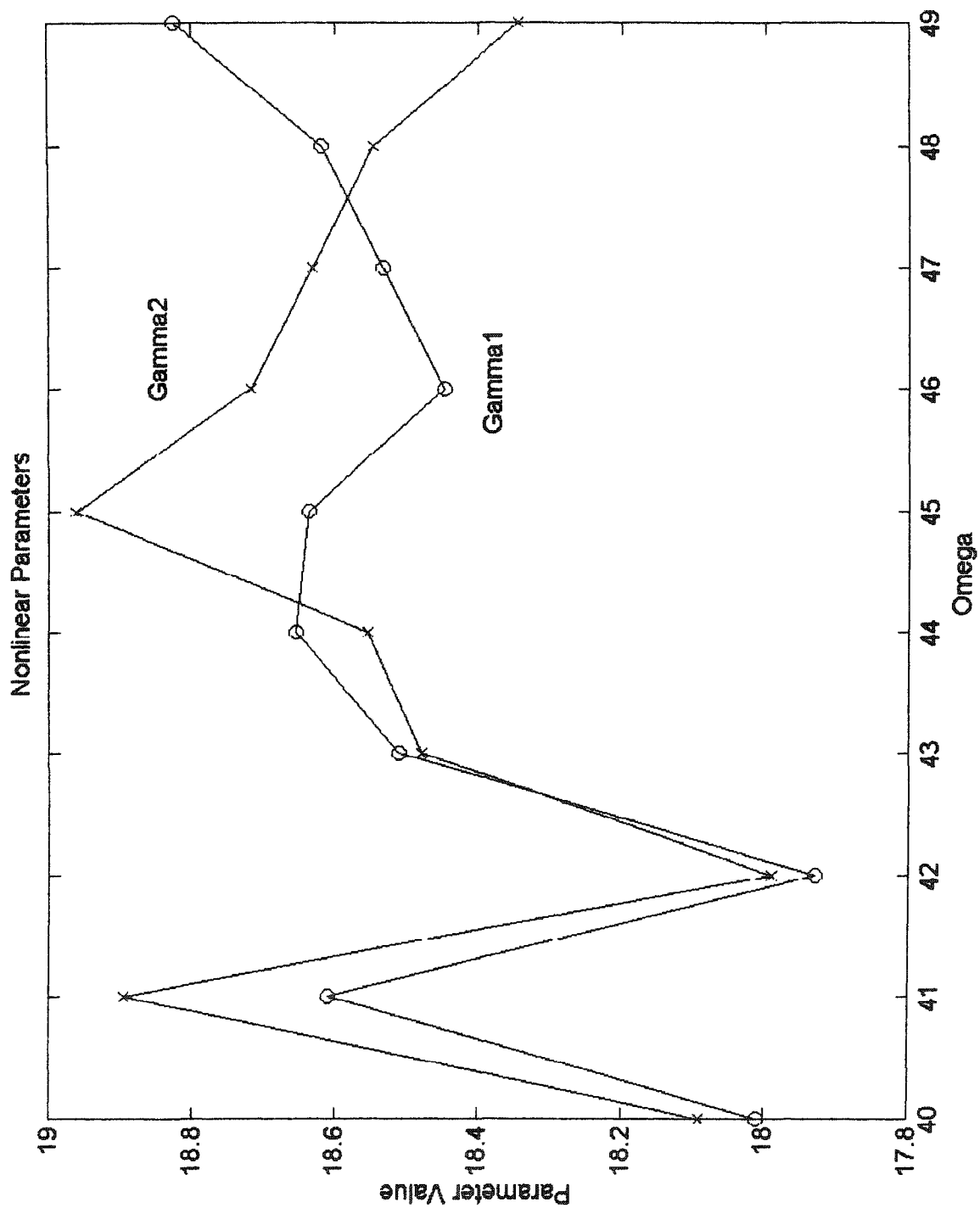


Table 5: Convergence pattern for the  $1^1S$  state, where Ratio =  $[\text{Energy}(\Omega - 2) - \text{Energy}(\Omega - 1)] / [\text{Energy}(\Omega - 1) - \text{Energy}(\Omega)]$ ,  $\Omega = N + \Omega_1$ , and  $NV$  is total number of basis functions.

$\Omega$	$NV$	Energy	Difference ( $\times 10^7$ )	Ratio
42	33	-0.597 138 979 257 696 807 296 095 1		
43	57	-0.597 139 061 191 160 229 487 982 2	0.819780857803310383	
44	90	-0.597 139 062 954 250 154 856 868 9	0.017640501341382384	46.47
45	134	-0.597 139 063 120 531 138 258 259 7	0.001663715428539411	10.60
46	190	-0.597 139 063 123 316 985 447 177 6	0.000027873644086935	59.69
47	260	-0.597 139 063 123 402 568 522 507 9	0.000000856296853292	32.55
48	345	-0.597 139 063 123 404 987 310 248 5	0.000000024201050536	35.38
49	447	-0.597 139 063 123 405 072 038 077 8	0.000000000847739735	28.55
50	567	-0.597 139 063 123 405 074 674 920 3	0.000000000026382785	32.13
51	707	-0.597 139 063 123 405 074 825 965 5	0.000000000001511275	17.46
52	868	-0.597 139 063 123 405 074 834 205 4	0.000000000000082443	18.33
53	1052	-0.597 139 063 123 405 074 834 331 3	0.000000000000001260	65.43
	Extp	-0.597 139 063 123 405 074 834 337 7 $\pm$	0.000000000000000021	19.80

Table 6: Convergence pattern for the  $2^1S$  state, where Ratio =  $[\text{Energy}(\Omega - 2) - \text{Energy}(\Omega - 1)] / [\text{Energy}(\Omega - 1) - \text{Energy}(\Omega)]$ ,  $\Omega = N + \Omega_1$ , and  $NV$  is total number of basis functions.

$\Omega$	$NV$	Energy	Difference ( $\times 10^5$ )	Ratio
39	20	-0.587 151 043 016 274 880 166 883 9		
40	40	-0.587 155 435 230 538 473 190 407 1	0.43946063382070798317	
41	70	-0.587 155 671 003 177 129 306 874 1	0.02359010444464016163	18.63
42	112	-0.587 155 678 540 275 385 078 560 3	0.00075412030877127698	31.28
43	168	-0.587 155 679 208 721 236 702 208 8	0.00006688098986069193	11.28
44	240	-0.587 155 679 212 575 658 166 058 3	0.00000038565206473551	173.42
45	330	-0.587 155 679 212 741 279 833 673 1	0.00000001657118679928	23.27
46	440	-0.587 155 679 212 746 648 695 753 4	0.00000000053717860539	30.85
47	572	-0.587 155 679 212 744 807 755 263 3	0.00000000001591461364	33.75
48	728	-0.587 155 679 212 746 811 406 396 6	0.00000000000036531218	43.56
49	910	-0.587 155 679 212 746 812 117 624 5	0.00000000000007116152	5.13
50	1015	-0.587 155 679 212 746 812 191 315 9	0.00000000000000737316	9.65
51	1240	-0.587 155 679 212 746 812 204 541 4	0.00000000000000132327	5.57
52	1496	-0.587 155 679 212 746 812 211 050 4	0.00000000000000065126	2.03
	Extp	-0.587 155 679 212 746 812 212 103 9 $\pm$	0.00000000000000017462	6.18



Table 7: Convergence pattern for the  $2^3P$  state, where  $\text{Ratio} = [\text{Energy}(\Omega - 2) - \text{Energy}(\Omega - 1)] / [\text{Energy}(\Omega - 1) - \text{Energy}(\Omega)]$ ,  $\Omega = N + \Omega_1$ , and  $NV$  is total number of basis functions.

$\Omega$	$NV$	Energy	Difference ( $\times 10^6$ )	Ratio
40	39	-0.596 872 821 718 250 761 308 813 5		
41	82	-0.596 873 728 191 903 938 736 750 9	0.9069673341510657765	
42	149	-0.596 873 738 113 177 432 232 436 1	0.0099266767878339460	91.37
43	244	-0.596 873 738 822 338 108 348 671 5	0.0007095468970856189	13.99
44	373	-0.596 873 738 832 029 635 193 740 5	0.0000096968050154738	73.17
45	540	-0.596 873 738 832 750 200 250 037 9	0.0000007209574882863	13.45
46	751	-0.596 873 738 832 762 355 097 488 8	0.0000000121614671875	59.28
47	1010	-0.596 873 738 832 764 668 787 743 6	0.0000000023149503299	5.25
48	1323	-0.596 873 738 832 764 729 560 271 5	0.000000000608056257	38.07
49	1694	-0.596 873 738 832 764 734 799 797 1	0.000000000052423792	11.60
	Extp	-0.596 873 738 832 764 734 958 938 6 $\pm$	0.000000000000430383	32.92

Table 8: Optimized nonlinear parameters for the  $1^1S$  state.

$\Omega$	$NV$	$\alpha^{(1)}$	$\beta^{(1)}$	$\gamma^{(1)}$	$\alpha^{(2)}$	$\beta^{(2)}$	$\gamma^{(2)}$
42	33	1.29828	0.40735	18.32544	1.15375	0.41833	19.53986
43	57	1.22168	0.50000	19.39575	1.17389	0.43097	18.86371
44	90	1.25781	0.89563	18.47211	1.16791	0.48340	19.37537
45	134	1.31140	0.59418	20.28973	1.18848	0.38226	19.57910
46	190	1.17108	0.85852	20.03717	1.10834	0.50781	19.78876
47	260	1.25067	1.02069	19.28625	1.16626	0.48297	18.98700
48	345	1.55286	1.03436	19.29443	1.19177	0.37036	18.99933
49	447	1.54388	1.12152	19.18494	1.17828	0.36896	19.31342
50	567	1.56165	1.28979	18.93579	1.16669	0.39282	19.41327
51	707	1.62518	1.40912	19.10522	1.22589	0.44189	18.63483
52	868	1.70325	1.45929	19.80695	1.20654	0.42932	19.41852
53	1052	1.71881	1.47198	19.98499	1.19287	0.42505	17.58771

Table 9: Optimized nonlinear parameters for the  $2^1S$  state.

$\Omega$	$NV$	$\alpha^{(1)}$	$\beta^{(1)}$	$\gamma^{(1)}$	$\alpha^{(2)}$	$\beta^{(2)}$	$\gamma^{(2)}$
39	20	1.44666	0.19421	16.93994	1.07129	0.30090	17.51099
40	40	1.21973	0.37360	16.52173	1.10480	0.38855	18.23834
41	70	1.52942	0.36084	16.59521	1.15802	0.35980	18.12958
42	112	1.46509	0.28693	16.85657	1.29797	0.34454	17.87927
43	168	1.16699	0.71899	17.65454	1.13068	0.59479	17.73370
44	240	1.30774	0.81104	17.18604	1.18115	0.60138	17.44489
45	330	1.53186	0.93195	16.53748	1.16290	0.58606	17.15076
46	440	1.73041	0.98584	16.49695	1.16766	0.56006	17.84485
47	572	1.64624	1.02795	18.02319	1.10980	0.56873	18.67334
48	728	1.57294	1.07166	20.45264	1.12164	0.57385	18.97449
49	910	1.55615	1.06024	20.23523	1.13361	0.58002	19.17627
50	1015	1.85406	1.16150	20.27728	1.13300	0.58105	19.16602
51	1240	1.84467	1.15662	20.25494	1.13519	0.58411	19.18842
52	1496	1.82593	1.14484	20.04578	1.14673	0.59021	19.38757

Table 10: Optimized nonlinear parameters for the  $2^3P$  state.

$\Omega$	$NV$	$\alpha^{(1)}$	$\beta^{(1)}$	$\gamma^{(1)}$	$\alpha^{(2)}$	$\beta^{(2)}$	$\gamma^{(2)}$
40	39	1.32092	0.36035	18.00983	0.79034	0.69275	18.09076
41	82	1.25488	0.44232	18.60919	0.70331	0.55835	18.89685
42	149	1.36938	0.51270	17.93054	0.81281	0.65179	17.98999
43	244	1.18353	0.69800	18.51025	1.00165	0.70929	18.47931
44	373	1.28961	0.69476	18.65588	1.05634	0.79230	18.55469
45	540	1.32507	0.76434	18.63800	0.90845	0.73566	18.96375
46	751	1.53662	0.82697	18.44684	0.88232	0.71698	18.71686
47	1010	1.52887	0.83118	18.53229	0.87836	0.71906	18.63306
48	1323	1.53650	0.83392	18.61951	0.87421	0.71570	18.54572
49	1694	1.53607	0.85156	18.82404	0.86407	0.71399	18.34418

## 7 Suggestions for Future Work

This work grew out of prior work on quantum three-body systems, and as such, would best be treated as a stepping stone for future projects. The excellent results achieved so far serve to emphasize the validity of this method for three-body systems with atomic mass ratios ranging from zero to approximately one. The first step would be (and is already underway) to determine the remaining low-lying energy levels of  $\text{H}_2^+$ . And then it should be possible and desirable to extend these calculation to more exotic systems (e.g., muonic systems) and to the isotopomers of the  $\text{H}_2^+$ , i.e.,  $\text{D}_2^+$  and  $\text{HD}^+$ .

In terms of computation, the Fortran coding presently in use is quite slow due to the triple summation required in the calculation of the radial integrals. At this time the slowness of calculation is not overly restrictive, but if one wishes to perform test calculations with large basis sets this may not be the case. The speed of computation, however, could be enhanced by resorting to recursion relations that have already been developed [59, 60].

Another avenue to be explored is the failure of the present wave functions in reproducing the nuclear-nuclear cusp condition as outlined by Kato [61]. One method that would at least begin to alleviate this problem is to include a number of terms in the expansion of the wave function with powers  $r_{12}^0$ . How many terms would be required, and which ones, remains to be determined, as is the accuracy of such an approach. Perhaps a more detailed study of the nature of the wave functions used in atomic theory will be in order.

As a final direction, these calculations lay a firm foundation for the calculation of relativistic and QED corrections, which are typically accurate to less than half as many significant figures as the nonrelativistic energy. This is one of the main motivations for pushing the accuracy of these energy calculations beyond that which is necessary for comparison with experiment. To this end, 48 or more digit precision could be used wherever needed through the use of different software packages [62, 32].

In addition, these relativistic and QED calculations are vitally important with respect to a metrological experiment being undertaken by Hilico and

colleagues [27, 63]. They propose to carry out a highly accurate frequency measurement of a multiphotonic transition between the two lowest states of  $\text{H}_2^+$  ( $v = 0, J = 0 \rightarrow v = 0, J = 1$ ) using Doppler-free spectroscopy. The main intent of this endeavour is to improve the proton to electron mass ratio  $m_p/m_e$  by a factor of 10. Alternatively, such a measurement could be used to study the theoretical relativistic and QED corrections for this ion.

## 8 Conclusion

The present variational calculations are important for a number of reasons. First, they represent the current benchmark results for the three lowest-lying states of the hydrogen molecule-ion  $\text{H}_2^+$ . Secondly, the method described in this work offers one the ability to systematically treat a wide range of three-body quantum systems, with very different mass ratios, from the same standpoint. The wave functions necessary for such a high-precision treatment are relatively compact, and depend upon only a small number of parameters that are easily optimized. Thirdly, these results represent an important step toward more fundamental metrological and QED calculations concerning  $\text{H}_2^+$ . In the end, it is hoped that the hydrogen molecule-ion, as the simplest molecule, will become as well understood as the helium atom.

# A Derivation of Operators in Hylleraas Coordinates

## A.1 Operator Relations

The relations needed to determine the explicit form of the operators  $\nabla_i^2$  and  $\nabla_1 \cdot \nabla_2$  are the following:

$$\hat{r}_1 \cdot \frac{\partial \hat{r}_1}{\partial r_1} = \frac{2}{r_1}, \quad (121)$$

$$\hat{r}_1 \cdot \frac{\partial}{\partial r_1} \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} = \frac{3}{r_{12}}, \quad (122)$$

$$\mathbf{r}_1 \cdot \nabla_1^Y = 0, \quad (123)$$

$$\nabla_1^Y = -\frac{\mathbf{l}_1^2}{r_1^2}, \quad (124)$$

as well as the triangular relation

$$r_{12}^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta. \quad (125)$$

We will now prove the first four of these relations. To do this we will make use of Cartesian and spherical polar coordinates, and the following rule for differentiating vectors:

$$\frac{\partial \mathbf{A}}{\partial u} = \frac{\partial A_1}{\partial u} \mathbf{i} + \frac{\partial A_2}{\partial u} \mathbf{j} + \frac{\partial A_3}{\partial u} \mathbf{k} \quad (126)$$

We begin with the first relation:

$$\begin{aligned} \hat{r}_1 \cdot \frac{\partial \hat{r}_1}{\partial r_1} &= \left\{ \frac{x_1}{r_1} \mathbf{i} + \frac{y_1}{r_1} \mathbf{j} + \frac{z_1}{r_1} \mathbf{k} \right\} \cdot \left\{ \frac{\partial}{\partial r_1} \frac{x_1}{r_1} \mathbf{i} + \frac{\partial}{\partial r_1} \frac{y_1}{r_1} \mathbf{j} + \frac{\partial}{\partial r_1} \frac{z_1}{r_1} \mathbf{k} \right\} \\ &= \frac{x_1}{r_1} \frac{\partial}{\partial r_1} \frac{x_1}{r_1} + \frac{y_1}{r_1} \frac{\partial}{\partial r_1} \frac{y_1}{r_1} + \frac{z_1}{r_1} \frac{\partial}{\partial r_1} \frac{z_1}{r_1} \\ &= \frac{x_1}{r_1} \left( \frac{1}{r_1} \frac{\partial x_1}{\partial r_1} - \frac{x_1}{r_1^2} \right) + \frac{y_1}{r_1} \left( \frac{1}{r_1} \frac{\partial y_1}{\partial r_1} - \frac{y_1}{r_1^2} \right) + \frac{z_1}{r_1} \left( \frac{1}{r_1} \frac{\partial z_1}{\partial r_1} - \frac{z_1}{r_1^2} \right) \\ &= \frac{x_1}{r_1} \left( \frac{1}{x_1} - \frac{x_1}{r_1^2} \right) + \frac{y_1}{r_1} \left( \frac{1}{y_1} - \frac{y_1}{r_1^2} \right) + \frac{z_1}{r_1} \left( \frac{1}{z_1} - \frac{z_1}{r_1^2} \right) \\ &= \frac{1}{r_1} - \frac{x_1^2}{r_1^3} + \frac{1}{r_1} - \frac{y_1^2}{r_1^3} + \frac{1}{r_1} - \frac{z_1^2}{r_1^3} \\ &= \frac{3}{r_1} - \frac{1}{r_1^3} (x_1^2 + y_1^2 + z_1^2) \\ &= \frac{3}{r_1} - \frac{1}{r_1^3} (r_1^2) \\ &= \frac{2}{r_1}. \end{aligned} \quad (127)$$

One may now use this result to determine the second relation; or it may be approached in the same way that we found the first relation. Choosing the former route, and noting that in Hylleraas coordinates  $r_1$  and  $r_{12}$  are independent variables, we may write

$$\begin{aligned}
\hat{r}_1 \cdot \frac{\partial \mathbf{r}_1}{\partial r_1} &= \hat{r}_1 \cdot \frac{\partial r_1 \hat{r}_1}{\partial r_1} \\
&= \frac{\hat{r}_1}{r_{12}} \left\{ \hat{r}_1 + r_1 \frac{\partial \hat{r}_1}{\partial r_1} \right\} \\
&= \frac{1}{r_{12}} + \frac{r_1}{r_{12}} \left( \hat{r}_1 \cdot \frac{\partial \hat{r}_1}{\partial r_1} \right) \\
&= \frac{1}{r_{12}} + \frac{r_1}{r_{12}} \frac{2}{r_{12}} \\
&= \frac{3}{r_{12}}.
\end{aligned} \tag{128}$$

For the third relation, we must remember that we originally wrote our wave function as the product  $\Psi = RY$ , and that  $\nabla_1^Y$  is defined to act only on the angular part of  $\Psi$ , i.e.,

$$\nabla_1^Y \Psi = R \nabla_1^Y Y,$$

and

$$\nabla_1^Y = \mathbf{i} \frac{\partial^Y}{\partial x_1} + \mathbf{j} \frac{\partial^Y}{\partial y_1} + \mathbf{k} \frac{\partial^Y}{\partial z_1}.$$

Rewriting the above in spherical polar coordinates and letting it act on  $\Psi$  gives

$$\begin{aligned}
\nabla_1^Y \Psi &= \mathbf{a}_{r_1} \frac{\partial^Y \Psi}{\partial r_1} + \mathbf{a}_{\theta_1} \frac{1}{r_1} \frac{\partial^Y \Psi}{\partial \theta_1} + \mathbf{a}_{\phi_1} \frac{1}{r_1 \sin \theta_1} \frac{\partial^Y \Psi}{\partial \phi_1} \\
&= R \mathbf{a}_{r_1} \frac{\partial^Y Y}{\partial r_1} + R \mathbf{a}_{\theta_1} \frac{1}{r_1} \frac{\partial^Y Y}{\partial \theta_1} + R \mathbf{a}_{\phi_1} \frac{1}{r_1 \sin \theta_1} \frac{\partial^Y Y}{\partial \phi_1} \\
&= R \mathbf{a}_{\theta_1} \frac{1}{r_1} \frac{\partial^Y Y}{\partial \theta_1} + R \mathbf{a}_{\phi_1} \frac{1}{r_1 \sin \theta_1} \frac{\partial^Y Y}{\partial \phi_1} \\
&= \mathbf{a}_{\theta_1} \frac{1}{r_1} \frac{\partial^Y \Psi}{\partial \theta_1} + \mathbf{a}_{\phi_1} \frac{1}{r_1 \sin \theta_1} \frac{\partial^Y \Psi}{\partial \phi_1},
\end{aligned}$$

where we have used the fact that  $Y$  is not a function of  $r_1$ , and  $\mathbf{a}_{r_1}$ ,  $\mathbf{a}_{\theta_1}$ , and  $\mathbf{a}_{\phi_1}$  are unit vectors in the indicated direction. The above allows us to express the operator  $\nabla_1^Y$  as

$$\nabla_1^Y = \hat{a}_{\theta_1} \frac{1}{r_1} \frac{\partial^Y}{\partial \theta_1} + \hat{a}_{\phi_1} \frac{1}{r_1 \sin \theta_1} \frac{\partial^Y}{\partial \phi_1}. \tag{129}$$

Knowing that  $\mathbf{r}_1 = r_1 \mathbf{a}_{r_1}$ , and  $\mathbf{a}_{r_1} \cdot \mathbf{a}_{\theta_1} = \mathbf{a}_{r_1} \cdot \mathbf{a}_{\phi_1} = 0$  leads directly to the desired relation

$$\mathbf{r}_1 \cdot \nabla_1^Y = 0. \quad (130)$$

We now turn our attention to the fourth relation. Using the operator expression just derived for  $\nabla_1^Y$  we may write

$$(\nabla_1^Y)^2 = \frac{1}{r_1^2 \sin \theta_1} \frac{\partial^Y}{\partial \theta_1} \left( \sin \theta_1 \frac{\partial^Y}{\partial \theta_1} \right) + \frac{1}{r_1^2 \sin^2 \theta_1} \left( \frac{\partial^Y}{\partial \phi_1} \right)^2. \quad (131)$$

But the square of the angular momentum vector in spherical polar coordinates is

$$l_1^2 = - \left\{ \frac{1}{\sin \theta_1} \frac{\partial}{\partial \theta_1} \left( \sin \theta_1 \frac{\partial}{\partial \theta_1} \right) + \frac{1}{\sin^2 \theta_1} \frac{\partial^2}{\partial \phi_1^2} \right\}, \quad (132)$$

which immediately implies the relation we set out to show:

$$\nabla_1^Y = - \frac{l_1^2}{r_1^2}. \quad (133)$$

We must also note that the above relations are also relevant under the exchange  $1 \rightarrow 2$ .

## A.2 Kinetic Energy Term

We may now use the relations found in Appendix A.1, and Eqs. (59) and (60), to derive the necessary expressions for the kinetic energy operator  $\nabla_1^2$  found in the Hamiltonian  $H$ . We proceed in the following manner:

$$\begin{aligned} \nabla_1^2 \Psi &= \nabla_1 \cdot \nabla_1 \Psi \\ &= \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \cdot \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \Psi \\ &= \hat{r}_1 \cdot \frac{\partial}{\partial r_1} \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \Psi \\ &\quad + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \cdot \frac{\partial}{\partial r_{12}} \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \Psi \\ &\quad + \nabla_1^Y \cdot \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \Psi \\ &= \hat{r}_1 \cdot \frac{\partial}{\partial r_1} \left\{ \hat{r}_1 \frac{\partial \Psi}{\partial r_1} \right\} + \hat{r}_1 \cdot \frac{\partial}{\partial r_1} \left\{ \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} \right\} + \hat{r}_1 \cdot \frac{\partial}{\partial r_1} \left\{ \nabla_1^Y \Psi \right\} \\ &\quad + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \cdot \frac{\partial}{\partial r_{12}} \left\{ \hat{r}_1 \frac{\partial \Psi}{\partial r_1} \right\} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \cdot \frac{\partial}{\partial r_{12}} \left\{ \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} \right\} \end{aligned}$$



$$\begin{aligned}
& + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \cdot \frac{\partial}{\partial r_{12}} \{ \nabla_1^Y \Psi \} \\
& + \nabla_1^Y \cdot \left\{ \hat{r}_1 \frac{\partial \Psi}{\partial r_1} \right\} + \nabla_1^Y \cdot \left\{ \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} \right\} + \nabla_1^Y \cdot \nabla_1^Y \Psi \\
= & \hat{r}_1 \cdot \left\{ \left( \frac{\partial \hat{r}_1}{\partial r_1} \right) \frac{\partial \Psi}{\partial r_1} + \hat{r}_1 \frac{\partial^2 \Psi}{\partial r_1^2} \right\} \\
& + \hat{r}_1 \cdot \left\{ \left[ \frac{\partial}{\partial r_1} \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \right] \frac{\partial \Psi}{\partial r_{12}} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}} \right\} \\
& + \hat{r}_1 \cdot \nabla_1^Y \frac{\partial \Psi}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \cdot \left\{ \hat{r}_1 \frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}} \right\} \\
& + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \cdot \left\{ (\mathbf{r}_1 - \mathbf{r}_2) \left( \frac{\partial}{\partial r_{12}} \frac{1}{r_{12}} \right) \frac{\partial \Psi}{\partial r_{12}} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial^2 \Psi}{\partial r_{12}^2} \right\} \\
& + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \cdot \left\{ \nabla_1^Y \frac{\partial \Psi}{\partial r_{12}} \right\} + (\nabla_1^Y \cdot \hat{r}_1) \frac{\partial \Psi}{\partial r_1} \\
& + (\nabla_1^Y \cdot \hat{r}_1) \cdot \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} + (\nabla_1^2 \cdot \hat{r}_1)^2 \Psi \\
= & \frac{2}{r_1} \frac{\partial \Psi}{\partial r_1} + \frac{\partial^2 \Psi}{\partial r_1^2} + \frac{3}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} + 2 \frac{\hat{r}_1 \cdot (\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}} \\
& - \frac{(\mathbf{r}_1 - \mathbf{r}_2)^2}{r_{12}^3} \frac{\partial \Psi}{\partial r_{12}} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)^2}{r_{12}^2} \frac{\partial^2 \Psi}{\partial r_{12}^2} - 2 \frac{(\mathbf{r}_2 \cdot \nabla_1^Y)}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} + (\nabla_1^Y)^2 \Psi \\
= & \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial \Psi}{\partial r_1} \right) + \frac{3}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} + 2(r_1 - r_2 \cos \theta) \frac{1}{r_{12}} \frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}} \\
& - (r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta) \frac{1}{r_{12}^3} \frac{\partial \Psi}{\partial r_{12}} + (r_1^2 + r_2^2 - 2r_1 r_2 \cos \theta) \frac{1}{r_{12}^2} \frac{\partial^2 \Psi}{\partial r_{12}^2} \\
& - 2 \frac{(\mathbf{r}_2 \cdot \nabla_1^Y)}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} + (\nabla_1^Y)^2 \Psi \\
= & \frac{1}{r_1^2} \frac{\partial}{\partial r_1} \left( r_1^2 \frac{\partial \Psi}{\partial r_1} \right) + \frac{1}{r_{12}^2} \frac{\partial}{\partial r_{12}} \left( r_{12}^2 \frac{\partial \Psi}{\partial r_{12}} \right) + 2(r_1 - r_2 \cos \theta) \frac{1}{r_{12}} \frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}} \\
& - 2 \frac{(\mathbf{r}_2 \cdot \nabla_1^Y)}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} + (\nabla_1^Y)^2 \Psi.
\end{aligned}$$

The expression for  $\nabla_2^2$  is obtained in an analogous manner.

### A.3 Mass Polarization Term

The only other operator of  $H$  in Eq. (27) that requires special attention is the mass polarization operator. Its determination is straightforward, although tedious, and is carried out in a manner similar to that shown for the kinetic energy terms in A.2:

$$\begin{aligned}
\nabla_1 \cdot \nabla_2 &= \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \cdot \left\{ \hat{r}_2 \frac{\partial}{\partial r_2} + \frac{(\mathbf{r}_2 - \mathbf{r}_1)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_2^Y \right\} \Psi \\
&= \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \cdot \hat{r}_2 \frac{\partial \Psi}{\partial r_2} \\
&\quad + \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \cdot \frac{(\mathbf{r}_2 - \mathbf{r}_1)}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} \\
&\quad + \left\{ \hat{r}_1 \frac{\partial}{\partial r_1} + \frac{(\mathbf{r}_1 - \mathbf{r}_2)}{r_{12}} \frac{\partial}{\partial r_{12}} + \nabla_1^Y \right\} \cdot \nabla_2^Y \Psi \\
&= \hat{r}_1 \cdot \hat{r}_2 \frac{\partial^2 \Psi}{\partial r_1 \partial r_2} + \hat{r}_2 \cdot (\mathbf{r}_1 - \mathbf{r}_2) \frac{1}{r_{12}} \frac{\partial^2 \Psi}{\partial r_2 \partial r_{12}} \\
&\quad + (\hat{r}_1 \cdot \nabla_2^Y) \frac{\partial \Psi}{\partial r_1} + (\hat{r}_2 \cdot \nabla_1^Y) \frac{\partial \Psi}{\partial r_2} \\
&\quad + \hat{r}_1 \cdot \frac{\partial}{\partial r_1} \left[ (\mathbf{r}_2 - \mathbf{r}_1) \frac{1}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} \right] \\
&\quad + (\mathbf{r}_1 - \mathbf{r}_2) \cdot (\mathbf{r}_2 - \mathbf{r}_1) \frac{1}{r_{12}} \frac{\partial}{\partial r_{12}} \left( \frac{1}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} \right) \\
&\quad + \nabla_1^Y \cdot (\mathbf{r}_2 - \mathbf{r}_1) \frac{1}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} + (\mathbf{r}_1 - \mathbf{r}_2) \cdot \nabla_2^Y \frac{1}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} + \nabla_1^Y \cdot \nabla_2^Y \Psi \\
&= \cos \theta \frac{\partial^2 \Psi}{\partial r_1 \partial r_2} + (r_1 \cos \theta - r_2) \frac{1}{r_{12}} \frac{\partial^2 \Psi}{\partial r_2 \partial r_{12}} \\
&\quad + (\hat{r}_1 \cdot \nabla_2^Y) \frac{\partial \Psi}{\partial r_1} + (\hat{r}_2 \cdot \nabla_1^Y) \frac{\partial \Psi}{\partial r_2} \\
&\quad + \hat{r}_1 \cdot \left\{ \frac{1}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} \frac{\partial}{\partial r_1} (\mathbf{r}_2 - \mathbf{r}_1) + (\mathbf{r}_2 - \mathbf{r}_1) \frac{1}{r_{12}} \frac{\partial^2 \Psi}{\partial r_1 \partial r_{12}} \right\} \\
&\quad + (2r_1 r_2 \cos \theta - r_1^2 - r_2^2) \left\{ \frac{1}{r_{12}^2} \frac{\partial^2 \Psi}{\partial r_{12}^2} - \frac{1}{r_{12}^3} \frac{\partial \Psi}{\partial r_{12}} \right\} \\
&\quad + \left\{ (\mathbf{r}_1 \cdot \nabla_2^Y) + (\mathbf{r}_2 \cdot \nabla_1^Y) \right\} \frac{1}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} + \nabla_1^Y \cdot \nabla_2^Y \Psi \\
&= \cos \theta \frac{\partial^2 \Psi}{\partial r_1 \partial r_2} + \left\{ (\mathbf{r}_1 \cdot \nabla_2^Y) + (\mathbf{r}_2 \cdot \nabla_1^Y) \right\} \frac{1}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} \\
&\quad - \left\{ (r_1 - r_2 \cos \theta) \frac{\partial}{\partial r_1} + (r_2 - r_1 \cos \theta) \frac{\partial}{\partial r_2} \right\} \frac{1}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} \\
&\quad + (\hat{r}_1 \cdot \nabla_2^Y) \frac{\partial \Psi}{\partial r_1} + (\hat{r}_2 \cdot \nabla_1^Y) \frac{\partial \Psi}{\partial r_2} - \frac{2}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} - \frac{\partial^2 \Psi}{\partial r_{12}^2} + \nabla_1^Y \cdot \nabla_2^Y \Psi \\
&= -\frac{1}{r_{12}^2} \frac{\partial \Psi}{\partial r_{12}} \left( r_{12}^2 \frac{\partial^2 \Psi}{\partial r_{12}^2} \right) + \cos \theta \frac{\partial^2 \Psi}{\partial r_1 \partial r_2} \\
&\quad + \left\{ (\mathbf{r}_1 \cdot \nabla_2^Y) + (\mathbf{r}_2 \cdot \nabla_1^Y) \right\} \frac{1}{r_{12}} \frac{\partial \Psi}{\partial r_{12}}
\end{aligned}$$

$$\begin{aligned}
& - \left\{ (r_1 - r_2 \cos \theta) \frac{\partial}{\partial r_1} + (r_2 - r_1 \cos \theta) \frac{\partial}{\partial r_2} \right\} \frac{1}{r_{12}} \frac{\partial \Psi}{\partial r_{12}} \\
& + (\hat{r}_1 \cdot \nabla_2^Y) \frac{\partial \Psi}{\partial r_1} + (\hat{r}_2 \cdot \nabla_1^Y) \frac{\partial \Psi}{\partial r_2} + \nabla_1^Y \cdot \nabla_2^Y \Psi.
\end{aligned} \tag{134}$$

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