

# Spin-free wave functions for small molecules

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## Abstract

In an earlier paper, we described a simple version of spin-free calculations of the energy of two 3-electron systems,  $HeH$  and  $H_3$ . Here, we extend our treatment to  $LiH^+$  and to two 4-electron systems,  $LiH$  and  $BeH^+$ . The necessary extensions are not trivial, but we are still able to obtain energies in atomic units consistent to at least four figures using very simple approximate wave functions. The wave functions used are given in the text, and are based on two-centre molecular orbitals consisting of exponential functions with varied exponents. Our procedures may be viewed as a convenient fusion of the classic valence-bond (VB) and molecular-orbital (MO) approaches to molecular structure.

# 1 Introduction

While it is regarded as self-evident that accurate (often numerical) solutions to the appropriate non-relativistic Schrödinger equation will provide full information on a wide variety of properties of any particular system, obtaining such solutions remains a challenging problem. Even more seriously, it remains difficult to interpret the calculations and to compare their theoretical predictions with recent high precision experiments

It therefore remains worthwhile to continue the long-standing search for relatively simple approximate wavefunctions which still provide physical insight. It is often possible to achieve fair accuracy for the energy  $E$  with these wavefunctions using much more limited variational procedures even though the corresponding solutions are necessarily less accurate.

A convenient means to obtain a spin-free approximate wavefunction  $\Psi$  for a general  $N$ -electron system is to begin with a simple *product* of  $N$  one-electron *space* orbitals  $\psi_i$  and to construct (using permutation operators) a suitable normalised projection operator  $T$ , so that  $T^2 = T$ , whose effect ensures that

$$T\Psi = T\psi_1(1)\psi_2(2)\dots\psi_N(N), \quad (1)$$

satisfies the Pauli principle for all pairs of electrons in the system. The general properties of such projectors  $T$  are well-known, the most important for our purposes being that  $T$  is constructed to be *Hermitian* and to *commute* with the Schrödinger Hamiltonian  $H$ , so that the usual variational energy calculation reduces significantly:

$$E \leq \frac{\langle T\Psi|HT\Psi \rangle}{\langle T\Psi|T\Psi \rangle} = \frac{\langle T\Psi|H\Psi \rangle}{\langle T\Psi|\Psi \rangle} \quad (2)$$

## 2 Spin Free Variational calculations

In [1] we outlined the theory of spin free quantum chemistry and derived projection operators appropriate to the ground state and some excited states of the 3 electron system  $HeH$ . Here, we extend the theory to four electron systems by constructing the appropriate projection operator. In subsequent sections we present calculations on both 3-electron and 4-electron systems.

Since  $H$  is a Hamiltonian symmetric in all space coordinates and independent

of spin, any permutation  $P$  of the variables commutes with  $H$  so that

$$[P, H] = 0 \Rightarrow \left[ \sum_k d_k P_k, H \right] = 0 \quad (3)$$

for any set of permutations. From this result we have that for any permutation  $P$

$$H\Psi = E\Psi \Rightarrow PH\Psi = HP\Psi = EP\Psi \quad (4)$$

so that either  $P\Psi = \Psi$  or  $P\Psi$  and  $\Psi$  are degenerate eigenfunctions of  $H$ . The sets of degenerate eigenstates can be classified by the permutation symmetries ( see [1] and [2]) and one way of describing this classification is using partitions of  $N$  in the form  $[\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_k]$ . The number  $n_1$  corresponds to the maximum number of coordinates that can be antisymmetrized in the wave function  $\Psi$ . Following this  $n_2$  is the maximum number of remaining coordinates that can be antisymmetrized and so on. This can be illustrated by a diagram of connected squares with the first column containing  $n_1$  squares, the second  $n_2$  and so on. Thus for example  $[\mathbf{N}]$  corresponds to a function antisymmetric in all *space* coordinates. In figure 1 we illustrate this for  $N = 3$  where we also associate coordinates with the boxes. A systematic way of constructing wave functions of the correct symmetry using projection operators is well known. ( See for example Musher [3]). The partition  $[\mathbf{2}, \mathbf{1}]$  is two-dimensional and simple choices of projection operators for the two diagrams are

$$C_1 = \frac{1}{3}(1 - P_{13})(1 + P_{12}) \quad \text{and} \quad C_2 = \frac{1}{3}(1 - P_{12})(1 + P_{13}) \quad (5)$$

respectively. In each of these products the factor of the form  $(1 - P_{ij})$  ensures that any wave function is antisymmetric in two coordinates and the factor of the form  $(1 + P_{ij})$  ensures that the wavefunction is not antisymmetric in all the coordinates so that they both produce a wave function with the symmetry  $[\mathbf{2}, \mathbf{1}]$ . However we can use any two *different choices of the 3 coordinates* in the boxes to construct a basis for the two-dimensional classification and we are free to choose a combination of these to form a wave function satisfying any given condition. In molecular calculations such a condition may be the symmetry on dissociation.

The permutation  $P$  is a permutation of the space coordinates and the corresponding permutation of spin coordinates,  $P^\sigma$ , also commutes with the spin-free hamiltonian  $H$  so that the spin function eigenstates can be classified in the same way. A *physically allowed* wave function also needs to

satisfy the Pauli Principle whereby if the total coordinates ( space and spin) of two electrons are interchanged then the wave function changes sign. Thus the physical wave function is a product of a space function with symmetries corresponding to a partition  $[\mathbf{n}_1, \mathbf{n}_2, \dots, \mathbf{n}_k]$  and a spin function with dual symmetries with a diagram related to the space function diagram but with the rows and columns interchanged. A proof of this result may be found in [1]. However the spin coordinates are constructed from products of  $\alpha$  – *spin* functions and  $\beta$  – *spin* functions and such a product cannot be antisymmetric in more than two coordinates. This restricts the physically allowed solutions. In the case of 3 electrons the spin function can only correspond to the partition  $[\mathbf{1}, \mathbf{1}, \mathbf{1}]$ , which is a completely symmetric function or  $[\mathbf{2}, \mathbf{1}]$  and consequently the space function can only correspond to  $[\mathbf{3}]$  or  $[\mathbf{2}, \mathbf{1}]$  respectively. Thus we can calculate the physically allowed energies independent of the spin variables using either of the partitions. In all of the calculations in this paper we will use a 2-electron core system and assume that for this core the electrons are completely symmetric. Thus for a 3 electron system dissociating to a one and a two electron system we require the latter to be symmetric in the space coordinates of two electrons. Such a dissociation is impossible for the partition  $[\mathbf{3}]$  which is antisymmetric in all 3 space coordinates so we will concentrate on solutions satisfying the symmetry  $[\mathbf{2}, \mathbf{1}]$  finding a solution which is also symmetric in the core coordinates. For a general function  $\Psi$  of the 3 coordinates we first construct

$$\Psi_1 = T_0\Psi = (1 + P_{12})\Psi \quad (6)$$

which is either zero or a function symmetric in the interchange of coordinates 1 and 2. We next construct  $\Psi_2 = T_1\Psi_1$  where

$$T_1 = (1 - P_{13}) + (1 - P_{23}) \quad (7)$$

Using either term in (7) ensures that we obtain a function corresponding to the partition  $[\mathbf{2}, \mathbf{1}]$  but the sum also ensures that the  $T_0$  and  $T_1$  commute and that the final product obtained is symmetric in coordinates 1 and 2. We can then construct the projection operator

$$T = \frac{1}{6}(2 - P_{13} - P_{23})(1 + P_{12}) \quad (8)$$

The numerical coefficient of the projection operator follows from the matrix representations of the permutation operators for the partition  $[\mathbf{2}, \mathbf{1}]$ ; it is not

needed in the calculations outlined below since the procedure is independent of the numerical value. Thus  $T\Psi$  is either zero or a function satisfying the correct symmetry and for a general  $\Psi$  we can calculate the variational estimate in (2) where the integration is over all  $N$  coordinates. (In general this involves integration over  $3N$  variables but the number of variables used is reduced in the examples below where the trial functions are independent of the azimuthal angles). This follows from  $T^2 = T$  and that for arbitrary functions  $g$  and  $f$

$$\begin{aligned} \langle f|(2 - P_{13} - P_{23})(1 + P_{12})g \rangle &= \langle (1 + P_{12})(2 - P_{13} - P_{23})f|g \rangle \\ &= \langle (2 - P_{13} - P_{23})(1 + P_{12})f|g \rangle \end{aligned} \quad (9)$$

In the case  $N = 4$  there are three physically allowed partitions:  $[\mathbf{2}, \mathbf{2}]$ ,  $[\mathbf{3}, \mathbf{1}]$  and the completely antisymmetric partition  $[\mathbf{4}]$ . Calculations in this paper are carried out for  $LiH$  and we use the same core representation as for  $N = 3$  constructed from an approximation of the ground state of  $(Li^+ + H^+)$  and the core function is symmetric in interchange of the two electrons so that the partition  $[\mathbf{4}]$  is not appropriate. The remaining electrons can be classified as *valence electrons* and an approximation using just these two electrons with complete shielding of the core is also symmetric in these two electrons. Thus we have considered the partition  $[\mathbf{2}, \mathbf{2}]$  which will allow both of these symmetries. The required projection operator  $T$  for  $N = 4$  is then

$$T = k((1 - P_{13})(1 - P_{24}) + (1 - P_{23})(1 - P_{14}))(1 + P_{34})(1 + P_{12}) \quad (10)$$

where  $k$  is a normalisation constant chosen so that  $T^2 = T$ . We note that in (10) the factors  $(1 + P_{12})$  and  $(1 + P_{34})$  commute between themselves and the remaining factor in  $T$ .

### 3 Three-electron System

In all the present calculations we divide the system into two sets of electrons : *core-electrons* ( with fixed parameters) and *valence -electrons*. The core system is a representation of  $(Li^+ + H^+)$  described using the variational principle with a trial function of the form

$$\Psi_0 = \exp(-\alpha r_{1A})\exp(-\beta r_{2A}) = \psi_1(1)\psi_2(2) \quad (11)$$

Table 1: Variational calculations for the ground state energy ( in a.u) of ( $Li^+ + H^+$ ) with symmetry  $[1, 1]$

R	$\alpha$	$\beta$	E	E+3/R
100	3.295	2.079	-7.260	-7.239
10	3.295	2.079	-7.449	-7.149
8	3.295	2.079	-7.499	-7.124
6	3.295	2.079	-7.582	-7.082
5	3.295	2.079	-7.648	-7.048
4	3.295	2.079	-7.749	-6.999
3	3.295	2.079	-7.915	-6.915
2	3.294	2.081	-8.248	-6.748

where the Lithium nucleus is denoted by A and the proton by B. We use atomic units (a.u) in all the calculations and assume that the distance between the two nuclei is R so that any two-centre integral can be calculated in spheroidal coordinates

$$p = \frac{r_a + r_b}{R}, \quad q = \frac{r_a - r_b}{R} \quad (12)$$

The Hamiltonian for the core system ( omitting the nuclear-nuclear term ) is

$$h_c = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{3}{r_{1a}} - \frac{1}{r_{1b}} - \frac{3}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}} \quad (13)$$

and we minimise

$$E = \frac{\langle T_0 \Psi_0 | h_c \Psi_0 \rangle}{\langle T_0 \Psi_0 | \Psi_0 \rangle}, \quad T_0 = \frac{1}{2}(1 + P_{12}) \quad (14)$$

The parameters  $\alpha$  and  $\beta$  in  $\psi_0$  depend on R and are given in table 1 for a range of R together with the corresponding energies E and E + 3/R. They do not vary very much with R except at smaller separations; at larger separations the energies approach approximations to the isolated Lithium ion similar to the well known open-shell approximation for the Helium atom. To treat the case of three electrons we include the single valence electron so that the Hamiltonian becomes

$$h_3 = h_c - \frac{1}{2}\nabla_3^2 - \frac{3}{r_{3a}} - \frac{1}{r_{3b}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \quad (15)$$

To obtain approximations for  $LiH^+$  we choose a trial function of the form

$$\hat{\Psi} = \psi_1(1)\psi_2(2)\psi_3(3),$$

$$\psi_3(3) = \exp(-aRp_3/2)\exp(bR(q_3/2)) \quad (16)$$

For this calculation the core parameters  $\alpha$  and  $\beta$  are fixed from the earlier calculation on  $(Li^+ + H^+)$  and the remaining parameters are varied. ( See Appendix 1 for a description of the numerical process).The form of the wave function reflects the dissociation product where we obtain the Lithium ion and a separate Hydrogen atom as expected for large R. The sign of b is not predetermined but for all R we have the constraint  $a > 0$  so that the wave function is normalisable .The results are presented in table 2.The pattern of the results follows previous calculations using valence bond theory with many terms [4] and large scale density function calculations [5]. We list the results in the special case  $a = b$  and for the more general case ( see Appendix 1 for the details of the approximation of the two-electron integrals and of the partial optimisation).In [4] an equilibrium is not found but a very shallow minimum is found in the more recent calculation in [5]. Our more general trial function indicates such a minimum at R about 4-5 atomic units and describes the important physical features of the wave function. If we impose the constraint  $b < 0$  so that the trial function is centred at A then for large R we obtain an approximation for the ground state of Lithium. However for the spherically symmetric Lithium atom, with no preferred direction, the exact wave functions are classified into s-states or p-states or states of higher angular momentum . Here we have a preferred direction and even if the effect of the proton on the energy is negligible, the direction affects the description of the wave function and the form of (16 ) does not correspond to a solution of an isolated Lithium atom where all directions are equivalent.

## 4 Four Electron Systems

In order to treat 4 -electron systems we use (2) with  $T$  now given by (10). We take  $\hat{\Psi}$  to have the form

$$\hat{\Psi} = \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4), \quad \psi_4(4) = \exp(-Rp_4/2)\exp(Rq_4/2) \quad (17)$$

Table 2: Variational Calculations for the ground state energy (in a.u) of  $LiH^+$  with symmetry  $[2, 1]$

R	E	$a = b$	E	a	b
10	-7.748	0.997	-7.747	0.997	0.978
8	-7.747	0.997	-7.747	0.997	0.978
7	-7.747	0.997	-7.747	0.997	0.978
6	-7.747	0.997	-7.748	1.080	0.925
5	-7.747	0.997	-7.749	1.080	0.925
4	-7.744	0.997	-7.749	1.080	0.925
3	-7.728	1.046	-7.735	1.080	0.925
2	-7.628	1.080	-7.627	1.067	0.993

First of all we consider the molecule  $LiH$ . Here  $\psi_1$  and  $\psi_2$  are the fixed core orbitals centred on the Lithium atom and  $\psi_3$  has the same form as in (16) with a and b variable parameters. The orbital  $\psi_4$  is the fixed hydrogen 1s orbital centred on the hydrogen atom. The results of varying a and b for  $LiH$  are given in table 4. Since  $-1 \leq q \leq 1$  with  $q = \pm 1$  denoting the values at the atoms then the *sign* of b indicates where the orbital is centred;  $b > 0$  denoting that the  $\psi_3$  has a maximum value at the hydrogen atom and  $b < 0$  that the maximum is on the Lithium atom. Thus b provides a measure of the charge distribution for any given R and hence the structure of the bond. McWeeny [6] points out that the usual descriptions of ionic or covalent bonds may be useful but *the structures do not exist except in our imagination* and do not correspond to any real structure. The sign of b provides a simple measure for the charge distribution and reflects the centre of charge of the orbital.

Note that it is not necessary that we choose  $\hat{\Psi}$  to be a product of orbitals. It may be any function of the coordinates of the 4 electrons. However the orbital concept has been found to be useful but molecular orbitals do not necessarily have the same form as atomic orbitals. Palke and Goddard [2] used a spin free approach and produced different orbitals where the valence orbital for  $LiH$  was nodeless between the atoms. This result is not surprising since if we use an approximate one dimensional model for the valence orbital, where the nuclei and the other electrons are approximated by local Coulomb potentials then the ground state wave function is nodeless. ( See



Appendix 2). The valence orbital will not necessarily be nodeless when the Pauli principle is taken into account and the potentials are non-local, but since the effects of the Pauli principle are small for large  $R$ , it is a reasonable approximation to use a trial function for the valence orbital that is nodeless between the atoms. Palke and Goddard obtained results from a multi-basis calculation that improve other calculations, such as Hartree Fock calculations for which the valence orbital has a node. They make the point that choosing the orbitals orthogonal, and hence producing a node, constrains the wave function and consequently leads to a higher energy for the ground state. This is also true for our calculations and the form of  $\psi_3$  used in (16) is completely nodeless.

Our results in table 3 follow closely previous calculations on  $LiH$  [2],[7],[8] indicating that the molecule dissociates into  $Li + H$  and has a minimum near  $R = 3$ . The experimental energy is  $E = -8.06$  at  $R = 3.015$  and at this value of  $R$  the results are very close to the values in table 3 with  $E = -7.992$ ,  $a = 0.669$ ,  $b = 0.363$  so that our energy is reproducing experiment to within an error of less than 1%. Gadea et al [8] have found similar results which are uniformly a little high and argue that this is mainly due to errors in the treatment of the core. Since we obtain the value  $E = -7.992$  for all  $R$  in the range  $3 < R < 3.1$  it is not possible to predict the exact value of  $R$  at equilibrium from our trial functions. To obtain higher accuracy it would be necessary to increase the complexity of both the core functions and the valence functions which usually involves using the terms  $r_{ij}$  explicitly in the trial functions. This was first shown by Hylleraas [9] in a treatment of atomic helium and more recently in [10] and [11] which treat  $H_3^+$  and atomic Lithium respectively using multi parameter trial functions.

Thus our simple wavefunction with at most 4 varying parameters leads to a good estimate of the equilibrium energy and in addition we can use it to calculate other properties. At  $R = 3.015$  we have used our solution to calculate the dipole moment. We obtain 5.840 which compares very favourably with the experimental value, 5.828 [8], and the value 5.645 obtained by Palke and Goddard [2].

We may use the same techniques to treat  $BeH^+$ . We need to construct the core orbitals,  $\psi_i, i = 1, 2$  in the same way as we did for  $LiH$  which implies we consider the completely symmetric state of  $(Be^{++} + H^+)$  and approximate the ground state as in (6). The parameters  $\alpha, \beta$  will be different and in table 4 we give results for a range of  $R$ ; in this range  $\alpha$  and  $\beta$  are essentially constant so that the change in energy arises from the interaction

Table 3: Variational Calculations for the ground state energy (in a.u.) of  $LiH$  with symmetry  $[2, 2]$

R	E	a	b
10	-7.926	0.357	-0.311
8	-7.931	0.397	-0.222
7	-7.937	0.425	-0.115
6	-7.946	0.446	-0.082
5	-7.967	0.449	0.043
4	-7.987	0.580	0.225
3	-7.992	0.674	0.369
2	-7.895	0.585	0.496

Table 4: Variational calculations for the ground state energy ( in a.u.) ( $Be^{++} + H^+$ ) with symmetry  $[1, 1]$

R	$\alpha$	$\beta$	E	E+4/R
1000	4.390	2.985	-13.6250	-13.6210
10	4.390	2.985	-13.8230	-13.4230
8	4.390	2.985	-13.8730	-13.3730
6	4.390	2.985	-13.9563	-13.2896
5	4.390	2.985	-14.0230	-13.2230
4	4.390	2.985	-14.1230	-13.1230
3	4.390	2.985	-14.2896	-12.9563
2	4.390	2.985	-14.6230	-12.6230

Table 5: Variational calculations for the ground state energy (in a.u.) of  $BeH^+$  with symmetry  $[2, 2]$

R	a	b	E
10	0.666	0.593	-14.7330
8	0.666	0.593	-14.7330
5	0.663	0.479	-14.7473
4	0.774	0.390	-14.7756
3	0.903	0.149	-14.8170
2.5	0.966	0.0834	-14.8240
2	1.007	-0.201	-14.7758

with the proton at a distance  $R$  from the nucleus of  $Be^{++}$ . The energy for the isolated ion  $Be^{++}$  is usually taken to be -13.6566 which is consistent with our results.

In table 5 we give the results for  $BeH^+$  where again the  $(Be^{++} + H^+)$  core is fixed and also we use the 1s orbital on the hydrogen atom so that only one orbital is varied and it is of the form given in (16). The variation of the energies with  $R$  is consistent to within 1% with previous work with the minimum near  $R = 2.5$  [13]. For this molecule the change of sign of the parameter  $b$  occurs for much smaller values of  $R$  reflecting the larger charge on the Beryllium core.

We conclude that these simple wave functions describe much of the chemistry and physics in these molecules. If more accurate values are required we may use these spin-free, symmetry adapted wave functions as zero order approximations in more accurate numerical calculations. To illustrate how we can improve the valence function we consider a more general trial function  $\hat{\Psi}$  where  $\psi_3$  is replaced by

$$\exp(-aRp/2)\exp(bRq/2)(1 + s(p - 1)\frac{R}{2})(1 + t(q + 1)\frac{R}{2}) \quad (18)$$

For  $LiH$  at  $R = 3$  (near the equilibrium point) with the values of  $a$  and  $b$  as in table 3 and the same level of approximation in the two-electron integrals, we obtain  $E = 7.995$ ,  $s = 0.050$ ,  $t = 0.103$ . Note that along the internuclear

axis between the nuclei ( $p = 1, -1 \leq q \leq 1$ ) we have  $\psi_3$  nodeless. This supports the observation of Palke and Goddard [2] and the node of this function on the internuclear axis is at  $q = -1, p = 1 - 2/(Rs)$ .

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## Appendix 1: Numerical procedures

### The Two Electron Integrals

The basic functions used in these calculations are easily expressed in spheroidal coordinates and almost all of the integrals required can be calculated exactly. The only exception are the two-electron integrals when the functions are centred on different atoms. For these we use the Neumann expansion in Legendre functions (with the azimuthal angles zero)

$$\frac{1}{r_{ij}} = \frac{2}{R} \sum_{n=0}^{\infty} A_n P_n(q_i) P_n(q_j) P_n(p_{<}) Q_n(p_{>}) \quad (19)$$

where  $p_{<}$  is the minimum of  $p_i$  and  $p_j$ ,  $p_{>}$  is the maximum of these variables and  $A_n = (2n + 1)$ . To illustrate the procedure used we consider  $N = 3$  and the integral

$$\int (T\Psi) \frac{1}{r_{12}} (p_1^2 - q_1^2)(p_2^2 - q_2^2) \Psi dV \quad (20)$$

We have

$$\Psi = \psi(1)\psi(2)\psi(3), \quad T\Psi = \frac{1}{6}(2 - P_{13} - P_{23})(1 + P_{12})\Psi \quad (21)$$

For fixed  $p_1, p_2$  we integrate over  $q_1$  and  $q_2$  using the Gauss-Legendre integration method, for sufficient number of terms in the expansion and the overlaps can be pre-calculated so as to produce a functions in the form  $g_n(p_1, p_2)$ . To complete the calculation we need to sum over terms in the form

$$\int_1^{\infty} \int_1^{p_2} g_n(p_1, p_2) P_n(p_1) Q_n(p_2) dp_1 dp_2$$

$$+ \int_1^\infty \int_1^{p_1} g_n(p_1, p_2) P_n(p_2) Q_n(p_1) dp_2 dp_1 \quad (22)$$

This integration is carried out using Gauss-Laguerre integration in both variables where the inner integrals are replaced by a difference of two infinite integrals. For example with fixed  $p_2$

$$\int_1^{p_2} g_n(p_1, p_2) P_n(p_1) dp_1 = \int_1^\infty g_n(p_1, p_2) P_n(p_1) dp_1 - \int_{p_2}^\infty g_n(p_1, p_2) P_n(p_1) dp_1 \quad (23)$$

This construction reduces the effect of the singularity of  $Q_n(p)$  when  $p = 1$  and for example the values of  $p_2$  in (23) can be chosen to be the Gauss-Laguerre integration points thus reducing the number of terms to be calculated. Furthermore, integrals involving only the orbitals not being optimised can be calculated prior to the optimisation. In [4] it was found necessary to use approximate, pre-calculated, values of the two-electron integrals so as to increase the speed of the optimisation. A similar technique is possible with our method by choosing how many terms are used in the Neumann expansion. The optimisation calculation can be carried out initially with a small number of terms and then the number increased for the final stages of the optimisation.

## The Optimisation Procedure

We use an approximate optimisation procedure which converges to a minimum value based on the assumption that the range of the non-linear and linear parameters are known. In each case the energy may be expressed in the form

$$E = E(s_1, s_2 \dots s_k) \quad (24)$$

where the  $s_i$  denote the parameters. This set includes any of the exponents of the exponentials or any additional quantities that are to be varied. The procedure is simply to choose a minimum from a sequence of evaluations of  $E$  for  $n$  from 1 to  $N_1$  where for each evaluation we choose

$$s_j = w_j(n\sqrt{u_j} - \text{int}[(n\sqrt{u_j})]) \quad (25)$$

Here  $w_j$  denotes the assumed range of the variable  $\text{int}[x]$  denotes the integer part of real number  $x$  and  $u_j$  is any chosen odd prime. The sequence  $\{n\sqrt{u_j} -$

$int[(n\sqrt{u_j})]$  as  $n$  varies is an equidistributed set of real numbers between 0 and 1 but to ensure that all the generated values of the  $s_j$  are independent it is necessary to choose a different odd prime for each  $j$ . This method is related to the standard Monte Carlo method and has the advantage that for each value of  $n$ , all the data points for the parameters are calculated so that the number of evaluations is reduced. Consequently the method is suitable for a many parameter calculation. However in this paper for each minimisation we only vary two parameters.

## Appendix 2

In order to construct a trial function orbital for interactions between two atomic systems we may approximate the atomic cores by local Coulomb potentials. Of course the considerations of the structure of the atomic systems and the consequences of the Pauli principle imply that the potentials will not be completely local but the use of the Coulomb core approximations provides a convenient way of assessing the form of any trial function used; it will be a better approximation at large  $R$  when the the effect of the constraints from the Pauli principle are small. In particular we are interested in the approximate nodal structure of the the trial function. The model problem is described by the Schrödinger equation

$$\left(-\frac{1}{2}\nabla^2 - \frac{\mu_a}{r_a} - \frac{\mu_b}{r_b}\right)\psi = E\psi \quad (26)$$

The parameters  $\mu_a, \mu_b$  are related to the shielding parameters for the atoms and we may write

$$\mu_a = (1+t)Z_a, \quad \mu_b = (1-t)Z_b, \quad -1 \leq t \leq 1 \quad (27)$$

Here  $Z_a, Z_b$  are the shielding parameters for the atoms and the model describes a set of Coulomb problems where  $t = 0$  corresponds to our physical system,  $t = 1$  describes a pure hydrogen-like atom at A and similarly  $t = -1$  describes a hydrogen atom at B. All of these Coulomb systems lead to generalised hydrogen-like molecular ion problems which have non-trivial solutions so that  $\psi \neq 0$  and we assume that the solutions  $\psi$  and  $E$ , are continuous in  $t$ .

For any fixed  $t$ , the solution of this equation separates in spheroidal coordinates so may write  $\psi = X(p)Y(q)$  where

$$((p^2 - 1)D_p^2 + 2pD_p + Rp(\mu_a + \mu_b) + \frac{ER^2p^2}{2})X = \delta X, \quad D_p = \frac{d}{dp} \quad (28)$$

and

$$((1 - q^2)D_q^2 - 2qD_q - Rq(\mu_a - \mu_b) - \frac{ER^2q^2}{2})Y = -\delta Y, \quad D_q = \frac{d}{dq} \quad (29)$$

Here  $\delta$  is the separation constant. These are two second-order differential equations which need to be solved simultaneously. But note that if for any value of  $q = q_0$

$$Y(q_0) = 0 = DY(q_0) \quad (30)$$

then by using a Taylor expansion about  $q_0$  we obtain  $Y$  identically zero for all  $q$ . This cannot occur since it implies that  $\psi$  is identically zero and hence we do not obtain a non-trivial solution. The same argument can be used for  $X$ . Now as  $t$  varies we have a sequence of problems and for  $t = 1$  we have the exact solution

$$X = \exp(-Z_a R(p - 1)), Y = \exp(-Z_a R(q + 1)) \quad (31)$$

so that  $\psi$  is nodeless. If at some value of  $t$ ,  $Y$  has a node then we may vary  $t$ , approaching 1, so that at some point the node vanishes. But this would mean that at this value of  $t$  both  $Y$  and  $D_q Y$  are zero which is a contradiction. Similarly if  $X$  has a node there is a value of  $t$  where  $X$  and  $D_p X$  are zero and again we have a contradiction. Thus we conclude that  $\psi$  remains nodeless for all values of  $t$ . Similar results have been established for one-electron problems in Merzbacher [10] and in Landau and Lifshitz [11]. Also the model problem has been treated by Burrows and Cohen [12] where the nodal structure was examined.

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Figure 1: The Partitions for  $N = 3$

