# Appendix E

# Mathematica [Wf] code for lower bounds
## by arbitrary choice without truncation

(*  This program solves for lower bounds of helium.

  user must enter "max", "a", "z",  and "lower"
  "max" is the maximum index for the one-particle basis set,  max = 0,1,2,3,... .
      The dimension of the two-particle space is then (max+1)^2
  "a" is a variational parameter
  "z" is the nuclear charge
  "lower" is the a priori lower bound to the base problem on the restricted Hilbert space.

  we first calculate the matrices for the following generalized matrix eigenvalue problem:

1) { ham11 + invrep ,     ham12    }      { I ,    0  }
   {    ham12     ,      ham22   }   = $\lambda$ { 0 , overlap }

  we then left-multiply both sides by the inverse of the right matrix:

2) { ham11 + invrep ,      ham12    }    { I , 0   }
   { invover * ham12 ,  invover * ham22 } = $\lambda$ { 0 , I   }

  we then replace "invbasis * ham22" with the diagonal matrix with
  "lower" on the diagonal.  Since we replace it totally we have no
  need to actually calculate "ham22" or "invbasis * ham22":

3) { ham11 + invrep ,     ham12    }      { I , 0  }
   { invover * ham12 ,   lower * I    }   = $\lambda$ { 0 , I   } *)


dim:= (max+1)^2               (* dimension of two-particle hamiltonian matrix *)

d[i_,j_]:=  If[i==j,1,0]       (* kronecker delta funcion *)

ham11:=      Table[h11[i,j],{i,1,dim},{j,1,dim}]
ham12:=      Table[h12[i,j],{i,1,dim},{j,1,2max+1}]
matrix:=     Table[mat[i,j],{i,1,dim+2max+1},{j,1,dim+2max+1}]
prematrix:=  Table[pre[i,j],{i,1,dim+2max+1},{j,1,dim+2max+1}]
square:=     Table[sqr[i,j],{i,1,2max+1},{j,1,2max+1}]

```
repulsion:=    Table[repulse[i,j],{i,1,dim},{j,1,dim}]
overlap:=      Table[over[i,j],{i,1,2max+1},{j,1,2max+1}]
final:=        Table[fin[i,j],{i,1,dim+2max+1},{j,1,dim+2max+1}]

v[m_,n_]:=     Simplify[-2a z(m+2)!(n+2)!/Sqrt[(n+1)(n+2)(m+1)(m+2)] *
               Sum[1*Sum[ (-1)^(c+k) (c+k+1)!/(c+2)!/(k+2)!/c!/k!/(m-c)!/(n-k)!
               ,{k,0,n}],{c,0,m}]]
```

(* m,n-th one-particle matrix element for the nuclear attraction term *)

```
t[m_,n_]:=     Simplify[(2a)^2 /2 (m+2)!(n+2)!/Sqrt[(n+1)(n+2)(m+1)(m+2)] *
                Sum[1*Sum[ (-1)^(c+k) (c+k+2)!/(c+2)!/(k+2)!/c!/k!/(m-c)!/(n-k)! *
                 ( (m+3)(n+3)/(k+3)/(c+3) -(m+3)/(c+3)/2 -(n+3)/(k+3)/2 + 1/4 )
                ,{k,0,n}],{c,0,m}]]
```

(* m,n-th one-particle matrix element for the radial kinetic energy term *)

```
vv[m_,n_]:=    Simplify[(-2a z)^2 (m+2)!(n+2)!/Sqrt[(n+1)(n+2)(m+1)(m+2)] *
                Sum[1*Sum[ (-1)^(c+k) (c+k)!/(c+2)!/(k+2)!/c!/k!/(m-c)!/(n-k)!
                ,{k,0,n}],{c,0,m}]]
```

(* m,n-th one-particle matrix element for the square of the nuclear attraction *)

```
tt[m_,n_]:=    Simplify[(2a)^4 /4 (m+2)!(n+2)!/Sqrt[(n+1)(n+2)(m+1)(m+2)] *
                Sum[1*Sum[ (-1)^(c+k) (c+k)!/(c+2)!/(k+2)!/c!/k!/(m-c)!/(n-k)! *
                 ( (c+k+1)(c+k+2)/16 - (m+n+4)(c+k+1)/4 + (n+3)(c+k+1)/(k+3)/4 +
                 (m+3)(c+k+1)/(c+3)/4 + (m+3)(n+3)/(k+3)/(c+3) + (m+2)(n+2) -
                 (m+2)(n+3)/(k+3) - (n+2)(m+3)/(c+3) )
                ,{k,0,n}],{c,0,m}]]
```

(* m,n-th one-particle matrix element for the square of the radial kinetic energy *)

```
vt[m_,n_]:=    Simplify[-z/2 (2a)^3 (m+2)!(n+2)!/Sqrt[(n+1)(n+2)(m+1)(m+2)] *
                Sum[1*Sum[ (-1)^(c+k) (c+k)!/(c+2)!/(k+2)!/c!/k!/(m-c)!/(n-k)! *
                 ( (m+3)(n+3)(c+k+1)/(k+3)/(c+3) -(m+3)(c+k+1)/(c+3)/2 –
                 (n+3)(c+k+1)/(k+3)/2 +(n+3)/(k+3) -1/2 + 1/4 (c+k+1) )
                ,{k,0,n}],{c,0,m}]]
```

(* m,n-th one-particle matrix element for the nuclear attraction potential times the
   kinetic energy.  This is also the n,m-th one-partile matrix element for the kinetic
   energy times the nuclear attraction potential *)

rep[m_,n_,s_,t_]:=    1/( 6a Sqrt[(m+1)(m+2)(n+1)(n+2)(s+1)(s+2)(t+1)(t+2)] ) *
                Sum[Sum[Sum[Sum[ (m+2)!(n+2)!(s+2)!(t+2)!/i!/j!/k!/l!/
                (i+2)!/(j+2)!/(k+2)!/(l+2)!/(m-i)!/(s-j)!/(n-k)!/(t-l)! *
                (-1)^(i+j+k+l) * (
          3 (k+l+3)! Sum[ (i+j+2+c)!/c!/(2^c) ,{c,0,k+l+3}] / (2^(i+j+3)) +
          (k+l+1)! Sum[ (i+j+4+c)!/c!/(2^c) ,{c,0,k+l+1}] / (2^(i+j+5)) +
          3 (i+j+3)! Sum[ (k+l+2+c)!/c!/(2^c) ,{c,0,i+j+3}] / (2^(k+l+3)) +
          (i+j+1)! Sum[ (k+l+4+c)!/c!/(2^c) ,{c,0,i+j+1}] / (2^(k+l+5))
                                )
             ,{l,0,t}],{k,0,n}],{j,0,s}],{i,0,m}]

(* {(max+1)m+n+1,(max+1)s+t+1}-th two-particle matrix element for the electron-
  electron repulsion term *)

Do[ repulse[(max+1)r+rr+1,(max+1)c+cc+1]= rep[r,rr,c,cc]
,{r,0,max},{rr,0,max},{c,0,max},{cc,0,max}]

(* constructs the (dim)X(dim) repulsion matrix *)

Do[ h11[(max+1)r+rr+1,(max+1)c+cc+1]= Simplify[t[r,c]d[rr,cc] + v[r,c]d[rr,cc] +
                t[rr,cc]d[r,c] + v[rr,cc]d[r,c] ]
,{r,0,max},{rr,0,max},{c,0,max},{cc,0,max}]

(* constructs the (dim)X(dim) base hamiltonian matrix *)

Do[ sqr[(max+1)r+rr+1,(max+1)c+cc+1]=
        Simplify[ 2( t[r,c]t[rr,cc] + v[r,c]v[rr,cc] ) +
        vt[r,c]d[rr,cc] + vt[rr,cc]d[r,c] + vt[c,r]d[rr,cc] + vt[cc,rr]d[r,c] +
        2( t[r,c]v[rr,cc] + t[rr,cc]v[r,c] ) +
        tt[r,c]d[rr,cc] + tt[rr,cc]d[r,c] + vv[r,c]d[rr,cc] + vv[rr,cc]d[r,c] ]
,{r,0,max},{rr,0,max},{c,0,max},{cc,0,max}]

(* constructs the matrix corresponding to the square of the hamiltonian - this
  is used in constructing the matrix ham12 *)

Do[ h12[(max+1)r+rr+1,cc+1]= Simplify[sqr[(max+1)r+rr+1,(max+1)c+cc+1] -
  Sum[ h11[(max+1)r+rr+1,(max+1)k+kk+1] h11[(max+1)k+kk+1,(max+1)c+cc+1]
  ,{k,0,max},{kk,0,max}]]
,{r,0,max},{rr,0,max},{c,0,0},{cc,0,max}]

(* constructs the first max+1 columns of matrix ham12 *)

```
Do[ h12[(max+1)r+rr+1,max+1+c]= Simplify[sqr[(max+1)r+rr+1,(max+1)c+cc+1] -
   Sum[ h11[(max+1)r+rr+1,(max+1)k+kk+1] h11[(max+1)k+kk+1,(max+1)c+cc+1]
   ,{k,0,max},{kk,0,max}]]
,{r,0,max},{rr,0,max},{c,1,max},{cc,0,0}]
```

(* constructs the next max columns of matrix ham12 *)

```
Do[ over[i,j]=h12[i,j] ,{i,1,max+1},{j,1,2max+1}]
```

(* constructs the first max+1 columns of matrix overlap *)

```
Do[ over[max+1+i,j]=h12[i(max+1)+1,j] ,{i,1,max},{j,1,2max+1}]
```

(* constructs the next max columns of matrix overlap *)

```
invover:= Inverse[N[overlap,60]]      (* defines the inverse of the matrix overlap *)
```

```
invrep:=  Inverse[N[repulsion,60]]    (* defines the inverse of the matrix repulsion *)
```

(* we now form the left-hand side matrix of equation 1 *)

```
Do[ mat[i,j]= N[h11[i,j] + invrep[[i,j]],60],{i,1,dim},{j,1,dim}]
```

```
Do[ {   mat[i,dim+j]= N[h12[i,j],60],
         mat[dim+j,i]= N[h12[i,j],60],
         mat[dim+i,dim+j]= 0,
     } ,{i,1,dim},{j,1,2max+1}]
```

(* we now form the inverse of the right-hand side matrix of equation 1 *)

```
Do[ pre[i,j]= 0
,{i,1,dim+2max+1},{j,1,dim+2max+1}]
```

```
Do[ pre[i,i]= 1
,{i,1,dim}]
```

```
Do[ pre[dim+i,dim+j]= invover[[i,j]]
,{i,1,2max+1},{j,1,2max+1}]
```

(* we now form a matrix consisting only of lower on the diagonal of the lower right
   quadrant and zero everywhere else *)

```
lowermat:=Table[low[i,j],{i,1,dim+2max+1},{j,1,dim+2max+1}]
```

Do[ low[i,j]=0 ,{i,1,dim+2max+1},{j,1,dim+2max+1}]

Do[ low[i,i]=lower ,{i,dim+1,dim+2max+1}]

(* we now form the final matrix which gives the matrix eigenvalue problem in eq.  3 *)

final= prematrix.matrix  + lowermat

Print["final",___,Eigenvalues[final//N]]

(* we now delete the block diagonal components of the final matrix and solve for the
   eigenvalues again.  This may give an estimate on how "big" the "mixing" between the
   finite dimensional matrix and the infinite dimensional matrix is.  *)

Do[ low[i,j]=0 ,{i,1,dim+2max+1},{j,1,dim+2max+1}]

Do[ { low[i,j+dim]= final[[i,j+dim]] ,  low[j+dim,i]= final[[j+dim,i]]
},{i,1,dim},{j,1,2max+1}]

Print["overlap",__,Eigenvalues[lowermat//N]]

# Appendix F

# Mathematica [Wf] code for Hylleraas
# variational calculations for two-electron atoms

(* This program calculates upper bounds for two-electron atoms and ions whose spatial
   function is symmetric and spin function is antisymmetric. The total wavefunction is
   antisymmetric and is just the product of the spatical and spin functions.  This being the
   case, and since our Hamiltonian is spin-free we ignore the spin function completely.  *)

(* ********** BEGINNING OF INTEGRAL CALCULATION *************** *)

(* Explanation of these formulas for the integrals is given in:

        R. A. Sack, C. C. J. Roothaan, and W. Kolos.  Recursive evaluation of some
          Atomic integrals.  Journal of Mathematical Physics.  8 (5) 1093-1094 (1967)

   In this program we do not form "kq","aq", or "jq" with any negative indices.  Negative
     Indices are found in integrals needed for lower bound calculations arising from the
     square of the Hamiltonian.

   According to their paper, our "2a" = their α, "2b" = β, "2c" = γ, "i" = "l",
     "j" = "m", and "k" = "n".  "kq" corresponds to their "Γ" and "aq" corresponds
     to their "B".  *)

```
Clear[aq,kq]
Table[ kq[i,j,k],{i,-1,lim},{j,-1,lim},{k,-1,lim3}];
Table[ aq[i,j,k],{i,-1,lim},{j,-1,lim},{k,-1,lim3}];
kq[0,0,0]:= 2/(2a+2b)/(2a+2c)/(2b+2c)
aq[0,0,0]:= 2/(2a+2c)/(2b+2c)

delta[x_,y_]:= If[x==y,1,0]

Do[ aq[i,j,k]= ( i aq[i-1,j,k] + k aq[i,j,k-1] + 2 delta[i,0] (j+k)! /
                (2b+2c)^(j+k+1) ) / (2a+2c)
,{i,0,lim},{j,0,lim},{k,0,lim3}]

Do[ kq[i,j,k]= ( i kq[i-1,j,k] + j kq[i,j-1,k] + aq[i,j,k] ) / (2a+2b)
,{i,0,lim},{j,0,lim},{k,0,lim3}]

Clear[aq]
```

Do[ jq[i,j,k]= kq[i,j,k]
,{i,0,lim},{j,i,lim},{k,0,lim3}]

Clear[kq]

jqqj[i_,j_,k_]:= kq[i,j,k]

(* this is the integral of x^i y^j z^k Exp[-(a x) -(b y) -(c z)] over {x,0,oo},{y,0,oo},
  {z,|x-y|,x+y}.  x = r1, y = r2, z = r12 .   Why do I do this strange assignment of
  jqqj = kq ?  It is just leftover from combining separate programs and later
  simplification *)

(* *************** END OF INTEGRAL CALCULATION ****************** *)

pow1:=  Array[p1,max];
(* p1[i] is the power of x=r1 in the unsymmetrized i-th basis function *)

pow2:=  Array[p2,max];
(* p2[i] is the power of y=r2 in the unsymmetrized i-th basis function *)

pow3:=  Array[p3,max];
(* p3[i] is the power of z=r12 in the unsymmetrized i-th basis function *)

mult:=  Array[mt,max];
(* mt[i] is the normalization constant for the symmetrized basis function *)

counter:=  0
Do[ { counter+=1 , p1[counter]=i , p2[counter]=j , p3[counter]=k }
, {i,0,9 },{j,i,9 },{k,0,6}]

hamiltonianmatrix:=  Table[hamiltonian[i,j],{i,1,max},{j,1,max}]

overlapmatrix:=       Table[overlap[i,j],{i,1,max},{j,1,max}]

norm[i_,j_,k_]:=       1 / Sqrt[ 8 Pi^2 jqqj[2i+1,2j+1,2k+1] ]

(* this is the normalization constant for the unsymmetrized basis function with
    x^i y^j z^k *)

over[i_,j_,k_,ii_,jj_,kk_]:= norm[i,j,k] norm[ii,jj,kk] * 8 Pi^2 jqqj[i+ii+1,j+jj+1,k+kk+1]

(* this is the overlap integral for two normalized but unsymmetrized basis functions *)

```
Do[ mt[i]=      1 / Sqrt[ over[p1[i],p2[i],p3[i],p1[i],p2[i],p3[i]] +
                         over[p1[i],p2[i],p3[i],p2[i],p1[i],p3[i]] +
                         over[p2[i],p1[i],p3[i],p1[i],p2[i],p3[i]] +
                         over[p2[i],p1[i],p3[i],p2[i],p1[i],p3[i]] ]
,{i,1,max}]
```

(* this calculates the normalization constant for the symmetrized i-th basis function *)

```
Do[ overlap[i,j]=   mt[i] mt[j] (        over[p1[i],p2[i],p3[i],p1[j],p2[j],p3[j]] +
                                         over[p1[i],p2[i],p3[i],p2[j],p1[j],p3[j]] +
                                         over[p2[i],p1[i],p3[i],p1[j],p2[j],p3[j]] +
                                         over[p2[i],p1[i],p3[i],p2[j],p1[j],p3[j]]    )
,{i,1,max},{j,i,max}]
```

(* this calculates the overlap integral for the symmetrized i-th and j-th basis functions *)

```
vnuc[i_,j_,k_,ii_,jj_,kk_]:=      - z 8 Pi^2 norm[i,j,k] norm[ii,jj,kk] *
                                  ( jqqj[i+ii,j+jj+1,k+kk+1] + jqqj[i+ii+1,j+jj,k+kk+1] )
```

(* this is the nuclear attraction integral for two unnormalized and unsymmetrized basis
   functions:  one with x^i y^j z^k and one with x^ii y^jj z^kk *)

```
teng[i_,j_,k_,ii_,jj_,kk_]:=      - 1/2 8 Pi^2 norm[i,j,k] norm[ii,jj,kk] (
    jqqj[i+ii+1,  j+jj+1,  k+kk+1   ] (a^2 +b^2 + 2 c^2)
  + jqqj[i+ii+1-1 ,j+jj+1  ,k+kk+1   ] (-2 a i -2 a -a k)
  + jqqj[i+ii+1   ,j+jj+1-1 ,k+kk+1   ] (-2 b j -2 b -b k)
  + jqqj[i+ii+1   ,j+jj+1   ,k+kk+1-1 ] (-4 c k -4 c -c i -c j)
  + jqqj[i+ii+1-2 ,j+jj+1   ,k+kk+1   ] (i(i-1) +2 i +i k)
  + jqqj[i+ii+1   ,j+jj+1-2 ,k+kk+1   ] (j(j-1) +2 j +j k)
  + jqqj[i+ii+1   ,j+jj+1   ,k+kk+1-2 ] (2k(k-1) +4 k + i k + j k)
  + jqqj[i+ii+1+1 ,j+jj+1   ,k+kk+1-1 ] a c
  + jqqj[i+ii+1   ,j+jj+1+1 ,k+kk+1-1 ] b c
  + jqqj[i+ii+1-1 ,j+jj+1   ,k+kk+1+1 ] a c
  + jqqj[i+ii+1   ,j+jj+1-1 ,k+kk+1+1 ] b c
  + jqqj[i+ii+1-2 ,j+jj+1   ,k+kk+1+1 ] (-c i)
  + jqqj[i+ii+1   ,j+jj+1-2 ,k+kk+1+1 ] (-c j)
  + jqqj[i+ii+1+1 ,j+jj+1   ,k+kk+1-2 ] (-a k)
  + jqqj[i+ii+1   ,j+jj+1+1 ,k+kk+1-2 ] (-b k)
  + jqqj[i+ii+1+2 ,j+jj+1-2 ,k+kk+1-2 ] (-j k)
  + jqqj[i+ii+1-2 ,j+jj+1+2 ,k+kk+1-2 ] (-i k)
  + jqqj[i+ii+1+2 ,j+jj+1-1 ,k+kk+1-2 ] b k
  + jqqj[i+ii+1-1 ,j+jj+1+2 ,k+kk+1-2 ] a k
  + jqqj[i+ii+1+2 ,j+jj+1-2 ,k+kk+1-1 ] c j
  + jqqj[i+ii+1-2 ,j+jj+1+2 ,k+kk+1-1 ] c i
```

```
    + jqqj[i+ii+1+2 ,j+jj+1-1 ,k+kk+1-1 ] (-b c)
    + jqqj[i+ii+1-1 ,j+jj+1+2 ,k+kk+1-1 ] (-a c)  )
```

(* this is the kinetic energy integral for two unnormalized and unsymmetrized basis
    functions:   one with x^i y^j z^k and one with x^ii y^jj z^kk *)

vrep[i_,j_,k_,ii_,jj_,kk_]:=    8 Pi^2 norm[i,j,k] norm[ii,jj,kk] jqqj[i+ii+1,j+jj+1,k+kk]

(* this is the electron-electron repulsion integral for two unnormalized unsymmetrized
    basis functions: one with x^i y^j z^k and one with x^ii y^jj z^kk *)

ham[i_,j_,k_,ii_,jj_,kk_]:=
        bb vnuc[i,j,k,ii,jj,kk] + aa teng[i,j,k,ii,jj,kk] + cc vrep[i,j,k,ii,jj,kk]


(* this forms the hamiltonian matrix element for two unnormalized and unsymmetrized
    basis functions: one with x^i y^j z^k and one with x^ii y^jj z^kk.  The constant aa, bb,
    and cc allow for one to vary the contributions from the kinetic energy, nuclear
    repulsion, and electron-electron repulsion, respectively.  For a two-electron atom one
    would have aa=bb=cc=1  *)

```
Do[ hamiltonian[i,j]= mt[i] mt[j] (    ham[p1[i],p2[i],p3[i],p1[j],p2[j],p3[j]] +
                                       ham[p1[i],p2[i],p3[i],p2[j],p1[j],p3[j]] +
                                       ham[p2[i],p1[i],p3[i],p1[j],p2[j],p3[j]] +
                                       ham[p2[i],p1[i],p3[i],p2[j],p1[j],p3[j]] )
,{i,1,max},{j,i,max}]
```

(* this calculates the upper triangular part of the hamiltonian matrix *)

```
Do[ { hamiltonian[i,j]=hamiltonian[j,i] , overlap[i,j]=overlap[j,i] }
,{i,2,max},{j,1,i-1}]
```

(* this fills in the lower triangular part of the hamiltonian and overlap matrices *)

N[Eigenvalues[ Inverse[N[overlapmatrix,90]].N[hamiltonianmatrix,90] ],4]

(* this solves for the eigenvalues *)

# Appendix G (preprint)

**Lower bound problems and bounds to atomic ionization energies**

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**Abstract*:*** A simple extension of a method by Calogero and Marchioro for constructing lower bound problems for ground states of systems of indistinguishable particles is applied to atomic systems. Their method is extended to yield an improved lower bound problem, which raises the ground state estimate and yields non-trivial lower bounds to excited states that were previously inaccessible, by their method. Rigorous upper bounds to atomic ionization energies are also derived.

## 1. Introduction

Lower bounds to energy eigenvalues of atomic systems have long been sought to complement the upper bounds of Rayleigh-Ritz calculations. These would allow the desired eigenvalues to be bracketed in certain intervals. They would also give quantitative information on how close approximate energy eigenfunctions are to the true eigenfunctions [1].

Previous reports on bounds to atomic ionization energies are few. Angulo, et.al. [2,3] have derived several rigorous equations involving radial moment expectation values which continues work started by Hoffmann-Ostenhof and Hoffmann–Ostenhof [4], while Seco, et.al., [5] have derived general bounds which show the power dependence of the nuclear charge, $Z$. In this note, a simple extension of a method introduced by Calogero and Marchioro [6] is used to construct comparison operators to obtain rigorous bounds to atomic ionization energies. Although we discuss only fermions in this note, the ideas apply also to bosons with trivial modification.

## 2. The lower bound problem

The wavefunctions of atomic and molecular systems are restricted to be antisymmetric in order that the electrons be indistinguishable and satisfy the Pauli

exclusion principle. Calogero and Marchioro showed how to take advantage of this property. In the space of antisymmetric functions, we are free to rearrange the particle indices of symmetric multi-particle operators without changing their expectation values. To illustrate how operators may be changed by rearranging particle indices, we consider the Hamiltonian of the lithium atom.

Let $H_0(i) = T(i) + V_{nuc}(i)$ be the hydrogenic one-electron operator on the $i$th electron and $R(i,j) = 1/r_{ij}$ be the two-electron repulsion operator acting on the $i$th and $j$th electrons (atomic units are used throughout). Using tensor product notation for clarity, we can rewrite the Hamiltonian as follows without changing its expectation value:

$$\langle H(1,2,3)\rangle = \left\langle \begin{array}{c} H_0(1)\otimes I(2)\otimes I(3) \ + \ I(1)\otimes H_0(2)\otimes I(3) \ + \ I(1)\otimes I(2)\otimes H_0(3) \\ \\ + \ R(1,2)\otimes I(3) \ + \ R(1,3)\otimes I(2) \ + \ I(1)\otimes R(2,3) \end{array} \right\rangle = \langle H_1(1,2)\otimes I(3)\rangle$$

$$(1)$$

$$\text{where} \quad H_1(1,2) = \frac{3}{2}H_0(1)\otimes I(2) + \frac{3}{2}I(1)\otimes H_0(2) + 3R(1,2)$$

In the space of antisymmetric three-electron functions, the two operators, $H(1,2,3)$ and $H_1(1,2)\otimes I(3)$, have identical expectation values. However, the revision becomes useful because we can relate the lowest eigenvalue of $H(1,2,3)$ to that of $H_1(1,2)$ directly, and thereby work in two-particle space.

## 2.1. The ground state

We define $\mathbf{H}_{M<N}^{N}$ as the $N$-particle Hilbert subspace where the first $M$ particles are antisymmetric in their coordinates. Note that $\mathbf{H}_{N}^{N}$ is a subspace of $\mathbf{H}_{N-1}^{N}$, and that $\mathbf{H}_{N-1}^{N} = \mathbf{H}_{N-1}^{N-1}\otimes\mathbf{H}$, where we denote $\mathbf{H} = \mathbf{H}_{1}^{1}$.

We minimize expectation values, using the previous decomposition of the lithium Hamiltonian as an example, and propose:

$$\min_{\substack{\Gamma\in\mathbf{H}_3^3 \\ \Gamma\neq0}}\frac{\langle\Gamma|H(1,2,3)|\Gamma\rangle}{\langle\Gamma|\Gamma\rangle} = \min_{\substack{\Gamma\in\mathbf{H}_3^3 \\ \Gamma\neq0}}\frac{\langle\Gamma|H_1(1,2)\otimes I(3)|\Gamma\rangle}{\langle\Gamma|\Gamma\rangle} \geq \min_{\substack{\Psi\in\mathbf{H}_2^3 \\ \Psi\neq0}}\frac{\langle\Psi|H_1(1,2)\otimes I(3)|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \min_{\substack{\Phi\in\mathbf{H}_2^2 \\ \Phi\neq0}}\frac{\langle\Phi|H_1(1,2)|\Phi\rangle}{\langle\Phi|\Phi\rangle} \quad (2)$$

The first equality results trivially from the antisymmetric nature of the trial functions, and the inequality results from the fact that $\mathbf{H}_3^3$ is a subspace of $\mathbf{H}_2^3$;

thus we are minimizing over a larger space of functions and the minimum can only decrease or remain the same.

The last equality requires more explanation. We denote the set (not subspace) of *all* eigenfunctions (not just those of unit norm) of an operator $A$ as $S[A]$; and $S[A]^c$ as the set of all functions in the domain of $A$ that are *not* eigenfunctions of $A$, i.e. the set complement of $S[A]$. We can decompose $\mathbf{H}_2^3$ into the union of two sets:

$$\mathbf{H}_2^3 = \mathbf{H}_2^2 \otimes \mathbf{H} = \left(S[H_1(1,2)] \times \mathbf{H}\right) \cup \left(S[H_1(1,2)]^c \times \mathbf{H}\right),$$

where $S[H_1(1,2)] \times \mathbf{H}$ is short-hand notation for the uncountable union, $\bigcup\limits_{g \in \mathbf{H}} \left(S[H_1(1,2)] \times \boldsymbol{g}(3)\right)$.

Any element, $f \in S[H_1(1,2)] \times \mathbf{H}$, can be written as $f = \phi(1,2) \times \gamma(3)$, where $\phi(1,2) \in \mathbf{H}_2^2$ is an eigenfunction of $H_1(1,2)$ and $\gamma \in \mathbf{H}$. It is obvious that $f \in S[H_1(1,2) \otimes I(3)]$ also. Similarly, any element, $g \in S[H_1(1,2)]^c \times \mathbf{H}$, can be written as $g = \phi(1,2) \times \gamma(3)$, where $\phi(1,2) \in \mathbf{H}_2^2$ is *not* an eigenfunction of $H_1(1,2)$ and $\gamma \in \mathbf{H}$. It then follows that $g \notin S[H_1(1,2) \otimes I(3)]$. We conclude that

$$S[H_1(1,2)] \times \mathbf{H} = S[H_1(1,2) \otimes I(3)] .$$

We now reformulate the last equality in (2) by minimizing only over the eigenfunctions (which gives the same minimum when the eigenvalues are below the continuous spectrum):

$$\min_{\substack{\Psi \in \mathbf{H}_2^3 \\ \Psi \neq 0}} \frac{\langle \Psi | H_1(1,2) \otimes I(3) | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \min_{\substack{\Psi \in S[H_1(1,2)] \times \mathbf{H} \\ \Psi \neq 0}} \frac{\langle \Psi | H_1(1,2) \otimes I(3) | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \min_{\substack{\Phi \in S[H_1(1,2)] \\ \Phi \neq 0}} \frac{\langle \Phi | H_1(1,2) | \Phi \rangle}{\langle \Phi | \Phi \rangle} = \min_{\substack{\Phi \in \mathbf{H}_2^2 \\ \Phi \neq 0}} \frac{\langle \Phi | H_1(1,2) | \Phi \rangle}{\langle \Phi | \Phi \rangle}$$

Equality of the minimums follows immediately since

$$\langle \Phi(1,2) | H_1(1,2) | \Phi(1,2) \rangle = \langle \Phi(1,2) \times \boldsymbol{g}(3) | H_1(1,2) \otimes I(3) | \Phi(1,2) \times \boldsymbol{g}(3) \rangle$$
$$\text{for all } \boldsymbol{g} \in \mathbf{H} \text{ and } \Phi(1,2) \in S[H_1(1,2)] .$$

It is now apparent that we can work with $H_1(1,2)$ directly instead of $H_1(1,2) \otimes I(3)$ to get lower bounds to the ground state of the true Hamiltonian. This is convenient because the two-particle problem can be solved much more accurately than the three-electron problem. We should stress that what we have done is construct an eigenvalue problem simpler than the original one, and the

lowest eigenvalue of the new problem is guaranteed to be lower that that of the original problem. We have not introduced a method for obtaining lower bounds to a given eigenvalue problem; rather, we have introduced a new problem, and must use existing methods to determine its eigenvalues.

A variational calculation (described in Appendix A) showed that the lowest eigenvalue of $H_1(1,2)$ is $\mathbf{l}_1 = -8.79\,hartree$. This is a poor lower bound to the ground state energy of the lithium atom, which is known to be –7.48 *hartree* [7].

So far we have considered the ground state only. The above derivation shows that for the ground state we can use the operator $H_1(1,2)$ instead of $H_1(1,2) \otimes I(3)$. However, for excited states, the derivation does not apply and we must work with $H_1(1,2) \otimes I(3)$ to ensure that we obtain lower bounds. The ground state of $H_1(1,2) \otimes I(3)$ is infinitely degenerate due to the identity operator on the third particle (i.e. $\lambda_1 = \lambda_2 = \lambda_3 = \ldots$). Thus the only lower bounds we can get for excited states are the same as for the ground state. Lack of consideration of this degeneracy can lead to erroneous lower bounds to excited states [8,9]

## 2.2. Extension to excited states

We now try a slightly different approach. By splitting the lithium atom Hamiltonian into two parts we are able employ Weyl's inequality [10] to improve the lower bound and also obtain non-trivial lower bounds to the excited state energy levels. Weyl's inequality states that given an operator of the form $H = A + B$, the eigenvalues are related by

$$\mathbf{l}^H_{i+j-1} \geq \mathbf{l}^A_i + \mathbf{l}^B_j, \quad i,j = 1,2,3,\ldots. \tag{3}$$

Calogero and Marchioro [6] also used this technique to look at lower bounds. However, they were unable to obtain bounds for excited states because both of their operators, *A* and *B* had lowest eigenvalues that were infinitely degenerate. We can avoid this difficulty by partitioning the lithium atom Hamiltonian in the following way:

$$\langle H(1,2,3) \rangle = \left\langle \begin{array}{c} H_0(1) \otimes I(2) \otimes I(3) \, + \, I(1) \otimes H_0(2) \otimes I(3) \, + \, I(1) \otimes I(2) \otimes H_0(3) \\[6pt] + \, R(1,2) \otimes I(3) \, + \, R(1,3) \otimes I(2) \, + \, I(1) \otimes R(2,3) \end{array} \right\rangle$$

$$= \left\langle A_c(1,2) \otimes I(3) + B_c(1,2,3) \right\rangle$$

where

$$A_c(1,2) = \frac{3c}{2} H_0(1) \otimes I(2) + \frac{3c}{2} I(1) \otimes H_0(2) + 3R(1,2)$$

and

$$B_c(1,2,3) = (1-c)\left( H_0(1) \otimes I(2) \otimes I(3) + I(1) \otimes H_0(2) \otimes I(3) + I(1) \otimes I(2) \otimes H_0(3) \right).$$

Note that $c$ is a parameter that can be chosen between 0 and 1 to obtain different partitioning.

Taking the case $c = 2/3$ as an example, the lowest eigenvalue of $A(1,2) \otimes I(3)$ (again determined by Hylleraas-type variational calculations) is $l_1^A = -4.75$ hartree, and is infinitely degenerate. The spectrum of $B(1,2,3)$ is one-third the spectrum of lithium without electron repulsion: $\{l_1^B = -3.38,\ldots,\ l_\infty^B = -3.00\}$hartree.

To use Weyl's inequality, we set $i = 1$, while varying $j$ in (3) to obtain $l_j^H \geq l_1^A + l_j^B$. The resulting lower bound spectrum for lithium is

$$\lambda_1 \geq -8.13,\ldots,\lambda_\infty \geq -7.75 \text{ hartree}$$

as opposed to the real spectrum

$$\lambda_1 = -7.48,\ldots,\ \lambda_\infty = -7.28 \text{ hartree}$$

Thus the ground state lower bound is improved and non-trivial bounds for the excited states are provided as well.

Figure 1 plots the lower bound to $l_1$ (lower line) and $l_\infty$ (upper line) as a function of c. When $c$ has its minimum value of zero, we recover the hydrogenic problem, which is uninteresting. When $c$ has its maximum value of 1, we recover our initial decomposition, $H_1(1,2) \otimes I(3)$ in defined in (1); this choice of $c$ is not optimal for the ground state and also does not allow the problem to yield lower bounds to excited states. This is clearly seen in figure 1, where it shows $l_\infty$ approaching $l_1$ as $c \to 1$. Varying $c$ from 2/3 does not significantly improve the bounds.

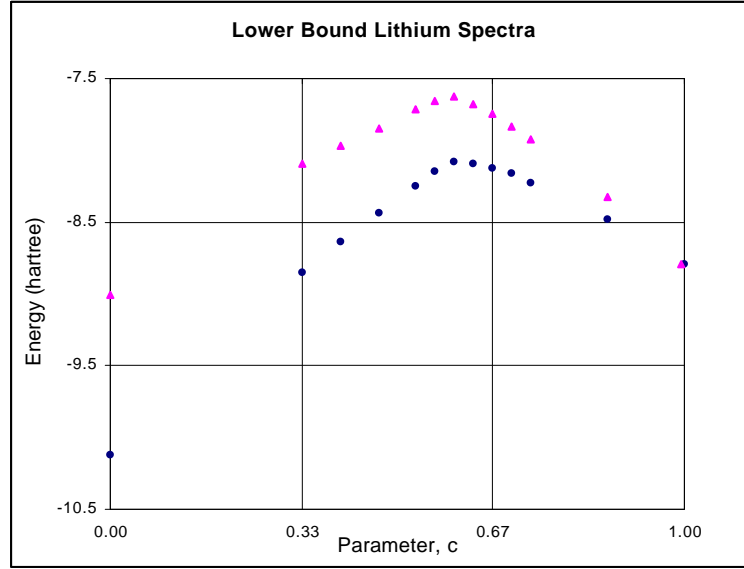Figure 1. Lower bounds to the ground state (•) and beginning of essential spectrum (▴) for the lithium atom are plotted against the parameter c.

Unfortunately, for all values of $c$, the lower bound for the beginning of the essential spectrum ($\lambda_\infty$) is below the true ground state of lithium ($\lambda_1$ = -7.48 hartree). This being the case, we did not pursue the matter further by replacing the Hylleraas-type upper bounds with rigorous lower bounds.

## 3. Bounds to ionization energies

We now derive several rigorous upper bounds for ionization energies. Letting $H^N$ be the $N$-particle atomic Hamiltonian and momentarily foregoing tensor product notation for brevity we have:

$$\left\langle H^N \right\rangle = \left\langle \sum_{i=1}^{N} H_0(i) + \sum_{i<j=1}^{N} R(i,j) \right\rangle = \left\langle \sum_{i=1}^{N-1} H_0(i) + \sum_{i<j=1}^{N-1} R(i,j) + H_0(N) + \sum_{i=1}^{N-1} R(i,N) \right\rangle$$

$$= \left\langle H^{N-1} + H_0(N) + \sum_{i=1}^{N-1} R(i,N) \right\rangle$$

Partitions like this have been used before to bound the ionization energy in terms of expectation values of general one-electron functions [4,11,12]. These authors did not, however, look for a bound of the form presented here.

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We define $E(N,Z)$ and $E_0(N,Z)$ as the $N$-electron ground state energy of an atom of nuclear charge $Z$ with and without electron-repulsion, respectively. We now minimize the expectation values as we did before, obtaining:

$$E(N,Z) = \min_{\Psi \in H_N^N} \langle \Psi | H^N(1,...,N) | \Psi \rangle$$

$$= \min_{\Psi \in H_N^N} \left[ \langle \Psi | H^{N-1}(1,...,N-1) \otimes I(N) | \Psi \rangle + \langle \Psi | I(1) \otimes ... \otimes I(N-1) \otimes H_0(N) + \sum_{i=1}^{N-1} R(i,N) | \Psi \rangle \right]$$

$$\geq \min_{\Psi \in H_N^N} \langle \Psi | H^{N-1}(1,...,N-1) \otimes I(N) | \Psi \rangle + \min_{\Psi \in H_N^N} \langle \Psi | I(1) \otimes ... \otimes I(N-1) \otimes H_0(N) + \sum_{i=1}^{N-1} R(i,N) | \Psi \rangle$$

$$\geq \min_{\Gamma \in H_{N-1}^{N-1}} \langle \Gamma | H^{N-1}(1,...,N-1) | \Gamma \rangle + \min_{\Psi \in H_N^N} \langle \Psi | I(1) \otimes ... \otimes I(N-1) \otimes H_0(N) + \sum_{i=1}^{N-1} R(i,N) | \Psi \rangle$$

$$= E(N-1,Z) + \min_{\Psi \in H_N^N} \langle \Psi | I(1) \otimes ... \otimes I(N-1) \otimes H_0(N) + \sum_{i=1}^{N-1} R(i,N) | \Psi \rangle$$

$$= E(N-1,Z) + \frac{1}{N} \min_{\Psi \in H_N^N} \langle \Psi | \sum_{i=1}^{N} I(1) \otimes ... \otimes I(i-1) \otimes H_0(i) \otimes I(i+1) \otimes ... \otimes I(N) + (N-1) \sum_{i=1}^{N} R(i,N) | \Psi \rangle$$

$$= E(N-1,Z) + \frac{1}{N} \min_{\Psi \in H_N^N} \langle \Psi | H_0^N + 2 \sum_{i<j=1}^{N} R(i,j) | \Psi \rangle \ > \ E(N-1,Z) + \frac{1}{N} \min_{\Psi \in H_N^N} \langle \Psi | H_0^N + \sum_{i<j=1}^{N} R(i,j) | \Psi \rangle$$

$$= E(N-1,Z) + \frac{1}{N} E(N,Z) \tag{4}$$

We can further this by bounding $E(N,Z)$ by $E_0(N,Z)$:

$$E(N,Z) \geq E(N-1,Z) + \frac{1}{N} E_0(N,Z) \tag{5}$$

Defining $I(N,Z)$ to be the ionization energy of an $N$-electron atom with nuclear charge $Z$, we find that (5) rearranges to

$$I(N,Z) = E(N-1,Z) - E(N,Z) \leq -\frac{1}{N} E_0(N,Z) \tag{6}$$

We can go further and formulate the bound of (6) as a general function of $N$ and $Z$. A lower bound of $-(3/2)^{1/3} Z^2 N^{1/3}$ is derived for $E_0(N,Z)$ in Appendix B. This yields

$$I(N,Z) \leq (3/2)^{1/3} Z^2/N^{2/3} \approx 1.145 \ Z^2/N^{2/3}$$

For neutral atoms, this reduces to

$$I(Z,Z) \leq 1.145 Z^{4/3} \tag{7}$$

This general bound can be compared to that of Seco, et. al. [5]. They initially reported that $I(Z,Z) \leq CZ^{4/3}$, but then immediately improved this to $I(N^3Z,Z) \leq CZ^{(4/3)(1-\alpha)} \approx CZ^{1.119}$ where $C$ is some undetermined constant and $\boldsymbol{a} = 9/56$. Bounds for ionization energies with $N < Z$ were not reported.

Angula, et.al., [2,3] reported many inequalities relating ionization energies to expectation values of powers of the radial distance. One that we will consider is:

$$I(N,Z) \leq \boldsymbol{e} = \left(\frac{Z}{N}\right)\left\langle\frac{1}{r}\right\rangle - \left(\frac{1}{2N^2}\right)\left\langle\frac{1}{r}\right\rangle^2 \tag{8}$$

where $\left\langle\dfrac{1}{r}\right\rangle = \int \dfrac{1}{r}\, \boldsymbol{r}(\vec{r})d\vec{r}$ , and $\boldsymbol{r}(\vec{r})$ is the electron density . While inequality (8) is rigorous, Angula, et.al. inserted an approximate expectation value for $1/r$, so the resulting *numerical* bounds they obtained for ionization energies are not rigorous. In Appendix C, we show that rigorous bounds for the expectation value are

$$-\frac{2E_0}{Z} > \left\langle\frac{1}{r}\right\rangle > -\frac{2E_{upper}}{Z} \tag{9}$$

where $E_0$ is the ground state energy of the atom's repulsionless Hamiltonian and $E_{upper}$ is the Hartree-Fock energy of the atom (or more generally, any upper bound). Substituting (9) into (8) we obtain a rigorous bound to the ionization energy:

$$I(N,Z) \leq \boldsymbol{e} = -\frac{2E_0}{N} - \frac{2E_{upper}^2}{Z^2 N^2} \tag{10}$$

The rigorous bounds given by (6), (7), and (10) are compared with experimental ionization energies [12] for the atoms He through Ne in Table 1.

**Table 1.** Upper bounds to ionization energies (in atomic units) for neutral atoms are tabulated for three different formulae. Experimental ionization energies are also given.

| $Z=N$ | $-E_0/N$ * | $1.145\, Z^2/N^{2/3}$ | $\varepsilon$ | $\varepsilon_{Exp}$ |
|-------|-----------|------------------------|---------------|---------------------|
| 2     | 2         | 2.9                    | 3.0           | 0.90                |
| 3     | 3.375     | 5.0                    | 5.4           | 0.20                |
| 4     | 5         | 7.3                    | 8.4           | 0.34                |
| 5     | 6.875     | 9.8                    | 11.9          | 0.31                |
| 6     | 9         | 12.5                   | 15.9          | 0.41                |
| 7     | 11.375    | 15.3                   | 20.3          | 0.53                |
| 8     | 14        | 18.3                   | 25.3          | 0.50                |
| 9     | 16.875    | 21.4                   | 30.8          | 0.64                |
| 10    | 20        | 24.7                   | 36.7          | 0.79                |

* These values are exact.

One immediate improvement can be made by starting with (4) instead of (5). This would improve the bound to

$$I(N,Z) \leq -E(N,Z)_{lower}/N .$$

Using the lower bounds for atomic ground states of Greenlee and Russell [13], we can improve our ionization bounds by 10-15%. In the case where the lower bounds converge to the exact energy, we get the best result:

$$I(N,Z) \leq -E(N,Z)_{exact}/N ,$$

which, unfortunately, is still an inequality; i.e. our bounds do not necessarily converge to the exact ionization energy.

Since the experimental ionization energies are far from our upper bounds, there is still plenty of room for improvement. It is hoped that future work will confirm the hypothesis that the ionization energy of atoms without electron repulsion is larger than that of real atoms. This seems very reasonable and would improve the bounds, but a rigorous proof does not yet exist.

## Appendix A: Variational Calculations

The variational calculations in this note were performed with *Mathematica* [14] using spatially symmetric Hylleraas-type functions of the form, $N_{l,m,n}(r_1^l r_2^m + r_1^m r_2^l)e^{-2r_1} e^{-2r_2} r_{12}^n$, where $N_{l,m,n}$ is a normalization constant. A total of 385 basis functions were used with $l$ and $m$ having the integer values 0 to 9, and $n$

from 0 to 6. Calculations of the ground state energies of He and Li$^+$ were also run to ensure accuracy. The results were $E$(He)= -2.90372437 and $E$(Li$^+$)= -7.2729913 hartree, which are in good agreement with other large variational calculations [15]. In obtaining the points plotted in figure 1, convergence became more difficult to achieve as $c$ decreased (although the point at $c$=0 is exact). All points shown had converged to the point that further improvements did not affect the graph.

For two-electron systems, the spin portion of the wavefunction can be separated from the spatial portion. For helium and two-electron ions the ground state wavefunction is known to be symmetric in the spatial coordinates and antisymmetric in the spin coordinates [16]. Small scale radial calculations on the problems in this paper (not restricted to a specific spin space), indicated to use the symmetric spatial coordinates in the Hylleraas calculations. Therefore, to calculate $l_1$ , only spatially symmetric trial functions were used in our calculations. Since the effective Hamiltonians are spin-free, there is no need to find the form of the spin part of the wavefunction.

## Appendix B: Lower Bounds to $E_0$

Letting $e_n = -\dfrac{Z^2}{2n^2}$ be the energy of a hydrogenic orbital of the principal quantum number $n$, and $w(n) = 2n^2$ be the degeneracy of $e_n$, we can derive the bound as follows:

$$-E_0(N,Z) \leq -\sum_{n=1}^{a} e_n w(e_n) = \sum_{n=1}^{a} \frac{Z^2}{2n^2} w(e_n) = Z^2 \sum_{n=1}^{a} \frac{2n^2}{2n^2} = aZ^2,$$

for some integer $a$. We must now pick $a$ so there are at least $N$ spin-orbitals occupied. For this it is sufficient to choose $a$ so that

$$N \leq \sum_{n=1}^{a} w(e_n) = \sum_{n=1}^{a} 2n^2 = \frac{a(a+1)(2a+1)}{3}$$

We can then write:

$$N \leq \frac{a(a+1)(2a+1)}{3} = \frac{a(a+1)(a+1/2)}{3/2} < \frac{(a+1)^3}{3/2}$$

$$\text{therefore,} \quad a > (3N/2)^{1/3} - 1$$

This does not guarantee that *a* is an integer solution; however, it is obvious that the smallest integer solution is contained in the interval $[(3N/2)^{1/3}-1, (3N/2)^{1/3}]$ so we can say that $a < (3N/2)^{1/3}$. This allows us to conclude that:

$$-E_0(N,Z) \leq Z^2 (3N/2)^{1/3}.$$

This bound has also been derived in a completely different way [17].

## Appendix C: Upper and Lower Bounds for $\langle 1/r \rangle$

Here we define $\left\langle \dfrac{1}{r} \right\rangle = \int \dfrac{1}{r} \boldsymbol{r}(\bar{r}) d\bar{r}$. We seek upper and lower bounds to this to make rigorous the following inequality [2,3]:

$$I(N,Z) \leq \varepsilon = Z\langle 1/r \rangle / N - \langle 1/r \rangle^2 / (2N^2)$$

Other inequalities given in their paper involve $\langle r \rangle$ and $\langle 1/r^2 \rangle$, which are difficult to bound; however, rigorous bounds can easily be found for $\langle 1/r \rangle$.

For atomic systems, the virial theorem relates the energy, *E*, to the expectation value of the potentials:

$$E = \langle V+R \rangle/2,$$

where *V* is the nuclear-attraction potential and *R* is the electron-repulsion potential. Since $V = -Z/r$ and *R* is positive, we immediately have:

$$E_{upper} > E = \langle V+R \rangle/2 > \langle V \rangle/2 = -Z\langle 1/r \rangle/2 .$$

Therefore, $\langle 1/r \rangle > -2E/Z > -2E_{upper}/Z,$

which is a lower bound due to Thirring [18]. In our application we will use Hartree-Fock energy values for $E_{upper}$. We can also obtain an upper bound. In the following the subscript zero refers to expectation values using the exact wavefunction of the repulsionless Hamiltonian.

$$E = \langle T \rangle + \langle V \rangle + \langle R \rangle > \langle T \rangle + \langle V \rangle \geq E_0$$

By the virial theorem, $\langle T \rangle = -E$ so that $-E + \langle V \rangle \geq E_0$

This gives $\langle -Z/r \rangle = \langle V \rangle \geq E_0 + E > 2 E_0 = \langle V \rangle_0$ to yield

$$\langle 1/r \rangle \ < \ -2 \, E_0 \, /Z$$

This is noteworthy in another respect: it shows that the nuclear attraction term is always greater in the real system when compared to the repulsionless system. This is not immediately obvious like the fact that the kinetic energy always decreases.

With these two bounds we can get rigorous bounds to the ionization energies of atoms using the inequalities of Angulo et. al. [2,3]. These are listed in Table 1, in the body of the paper. Below is Table 2, which shows the accuracy of the two bounds compared to the expectation value in the Hatree-Fock approximation [19].

**Table 2:** Bounds for $\langle 1/r \rangle$ (in atomic units) for neutral atoms. Also tabulated are the repulsionless and Hartree-Fock [21] ground state energies that were used to calculate the bounds.

| $Z=N$ | $-E_0{}^*$ | $-E_{HF}$ | $\langle 1/r \rangle_{Lower}$ | $\langle 1/r \rangle_{HF}$ | $\langle 1/r \rangle_{Upper}{}^*$ |
|---|---|---|---|---|---|
| 2 | 4 | 2.862 | 2.9 | 3.4 | 4 |
| 3 | 10.125 | 7.433 | 5.0 | 5.7 | 6.75 |
| 4 | 20 | 14.58 | 7.3 | 8.4 | 10 |
| 5 | 34.375 | 24.54 | 9.8 | 11.4 | 13.75 |
| 6 | 54 | 37.70 | 12.6 | 14.7 | 18 |
| 7 | 79.625 | 54.43 | 15.6 | 18.3 | 22.75 |
| 8 | 112 | 74.85 | 18.7 | 22.3 | 28 |
| 9 | 151.875 | 99.49 | 22.1 | 26.5 | 33.75 |
| 10 | 200 | 128.7 | 25.7 | 31.1 | 40 |

* These values are exact.

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# Appendix H (preprint)

## Remarks on the Effective Field Method and Weyl's Inequality

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**Abstract:** We show that the effective field method[1] for calculating lower bounds to eigenvalues is a special case of Weyl's inequality which allows us to conclude that it is incapable of giving lower bounds of a quality similar to Hartree-Fock upper bounds.

Upper bound atomic and molecular calculations have enjoyed tremendous success due to the simplicity of the variational theorem and the ease of Hartree-Fock calculations. Lower bound calculations, however, have proved very difficult and elusive, but are very desirable because without them, there is no *quantitative* measure of how close an approximate eigenvalue is to the true eigenvalue.

Let $A = A_0 + B$ be an operator where $A_0$ is a sum of single-particle operators and $B$ is a positive-definite many-particle operator. In many cases, the eigenvalues and eigenfunctions of $A_0$, called the base problem, can be easily and well approximated – sometimes even solved for exactly. The operator $B$ is viewed as a perturbation to $A_0$ which raises the eigenvalues. The idea behind the effective field method is to construct an operator less than $B$, call it $S$, which is of the simple form of a sum of single-particle operators and a constant. One can then solve the much simpler eigenvalue problem, $A_0 + S$, which will give lower bounds to the eigenvalues of $A$.

Based on work in the seventies on the stability of matter, Hertel, Lieb, and Thirring presented the effective field method with the hopes that it "promises to become as accurate as the Hartree-Fock procedure for the upper bound".[1] They derived a general expression for $S$ (as defined above) in terms of an essentially arbitrary function $f$ (called the repulsion potential) and a function $v$ (called the subsidiary potential) which is restricted to be less than $B$:

$$B \; > \; S \; = \; \Phi + C \; ,$$
$$\text{where} \;\; \Phi = \sum_{a=1}^{N} f(\mathbf{x}_a)$$

$$\text{and } \; C = -\frac{1}{2}\int \frac{d^3k}{(2p)^2}\left\{\frac{\tilde{\boldsymbol{f}}(\mathbf{k})^2}{\tilde{v}(\mathbf{k})} + Nv(\mathbf{k})\right\} > 0.$$

We denote $\tilde{f}(k)$ as the fourier transform of $f(x)$. The main task they performed was proving that the above form for the constant $C$ is sufficient to force $S < B$. Hertel, *et al.*, applied the effective field method to atoms and numerically solved for lower bounds to the ground state energies. Greenlee and Russell continued this work and were able to find a repulsion and subsidiary potential that allowed for lower bounds to atomic ground state energies to be solved for exactly.[2] While both works improved the lower bounds from the trivial bounds obtained from summing the hydrogenic eigenvalues according to the Pauli exclusion principle, both sets of lower bounds are still far from experimental and Hartree-Fock values.

The effective field method is really a special case of Weyl's inequality. Weyl's inequality states that for the eigenvalue problem, $A = A_0 + B$, we have

$$\boldsymbol{l}_{i+j-1}(A) \ge \boldsymbol{l}_i(A_0) + \boldsymbol{l}_j(B),$$

where $\lambda_i(A)$ is the $i$-th eigenvalue of the operator $A$. In the general case where the operator has no eigenvalues or the eigenvalues are not below continuous spectrum, $\lambda$ refers to the infimal point of the spectrum.

If we write the operator $A = A_0 + B$ instead as $A = (A_0+S) + (B-S)$, where $S$ is determined from the effective field method, then we know that the spectrum of $(B-S)$ lies above zero, so that Weyl's inequality gives

$$\boldsymbol{l}_i(A) \ge \boldsymbol{l}_i(A_0 + S) + \boldsymbol{l}_1(B - S) > \boldsymbol{l}_i(A_0 + S) = \boldsymbol{l}_i(A_0 + \Phi + C) = \boldsymbol{l}_i(A_0 + \Phi) + C \;.$$

We now we write $S = \Phi$, ignoring $C$ and not worrying about positive definiteness of $B$-$S$. We find that the constant $C$ arises naturally as a consequence of Weyl's inequality:

$$\boldsymbol{l}_i(A) \ge \boldsymbol{l}_i(A_0 + \Phi) + \boldsymbol{l}_1(B - \Phi) > \boldsymbol{l}_i(A_0 + \Phi) + C \;.$$

where $C$ is a lower bound to the lowest eigenvalue or spectral point of the operator $B$-$\Phi$. Thus $B$-$\Phi$-$C$ would be the positive definite operator originally proposed by Hertel, *et al*.

In many applications, $B$ is a multiplicative operator. If $\Phi$ is then also chosen as a multiplicative operator, then assuring that the spectrum of the *operator* $(B$-$\Phi)$ is bounded below is equivalent to showing that the *function* $(B$-$\Phi)$ is bounded below. This approach has been taken by Fleischhauer, et al., who obtained lower bounds for He (-3.390 a.u) and Li (-8.308 a.u.) to be compared with the experimental values for He (-2.9037 a.u.) and Li (-7.478 a.u.).[3] We extend this type of application to larger systems.

For atomic systems, the *N*-electron Hamiltonian is defined as $H = A_0 + B$ , where

$$A_0 = \sum_{i=1}^{N}\left(-\frac{1}{2}\Delta_i - \frac{Z}{r_i}\right) \text{ and } B = \sum_{i<j=1}^{N}\frac{1}{r_{ij}}.$$

The base problem, $A_0$, is a sum of one-particle operators, and is exactly solvable. Summing the one-electron eigenvalues according to the Pauli principle provides a rigorous lower bound to a multi-electron atom. This lower bound is very poor, however, because it ignores the electron-repulsion ($B$) which can only increase the energy.

In order that the modified eigenvalue problem be easy to solve, we choose $\Phi = (N\text{-}1)\sum_{i=1}^{N}f(r_i)$ so that $A_0 + \Phi$ reduces to $N$ one-particle problems. The other half of the problem is then

$$B - F = \sum_{i<j=1}^{N}\frac{1}{r_{ij}} - (N\text{-}1)\sum_{i=1}^{N}f(r_i) = \sum_{i<j=1}^{N}\left(\frac{1}{r_{ij}} - f(r_i) - f(r_j)\right).$$

All we need to do is find the minimum of $B - \Phi$. This will be $N(N\text{-}1)/2$ times greater than the minimum of $f(r_{ij}, r_i, r_j) = \frac{1}{r_{ij}} - f(r_i) - f(r_j)$ .

To make things simpler, we first replace $B$ with a simpler and lower potential $\sum_{i<j=1}^{N}\frac{1}{r_i + r_j}$ . This is easily seen to be less than $\sum_{i<j=1}^{N}\frac{1}{r_{ij}}$ by the triangle inequality ($r_i + r_j \geq r_{ij}$). Our function to minimize becomes a function only of two variables, $f(r_i, r_j) = \frac{1}{r_i + r_j} - f(r_i) - f(r_j)$ , and the minimum can now be found by simple plots.

We chose to work with $f(r_i) = a \, Exp[-br_i]$. By setting the partial derivatives of $f(r_i, r_j)$ equal to zero, one can show that local minimums for $f(r_i, r_j)$ lay on the $r_i = r_j$ axis. To find the global minimum, we must compare the local minimums to the values of $f(r_i, r_j)$ on the boundaries. Thus we made plots of $f(r_i, r_j = r_i)$ and $f(r_i, r_j = 0)$ with a variety of choices of **a** and **b**, recording the global minimum as $\Lambda(\alpha, \beta)$. The symmetry of $f(r_i, r_j)$ forces the plots $f(r_i, r_j = 0)$ and $f(r_i = 0, r_j)$ to be the same, so only one was checked. This gives:

$$B - \Phi = \sum_{i<j=1}^{N}\left(\frac{1}{r_{ij}} - ae^{-br_i} - ae^{-br_j}\right) \geq \sum_{i<j=1}^{N}\left(\frac{1}{r_i + r_j} - ae^{-br_i} - ae^{-br_j}\right)$$

$$\geq \sum_{i<j=1}^{N}\Lambda(a, b) = \frac{N(N-1)}{2}\Lambda(a, b)$$

We then add $\Phi$ to $A_0$ and solve for the eigenvalues of the resulting one-electron operator $H'$, where $Z$ is the nuclear charge:

$$H'\Psi \; = \; \left( -\frac{1}{2}\Delta \; -\frac{Z}{r} + (N-1)aE^{-br} \right)\Psi \; = l\,\Psi$$

The calculations were split into different angular momentum subspaces ($l = 0,1,2,\ldots$) so that several one-dimensional radial variational calculations were performed. Truncated sets of the total orthonormal set, $N(g,n)e^{-gr}L_n^2(2gr)$, were used, where $L_n^2(2gr)$ are associated Laguerre polynomials, $N(\gamma,n)$ is a normalization constant, $\gamma$ is a variational parameter, and $n$ is an integer. The lowest eigenvalue in the $l=0$ subspace converged almost immediately to more than 8 significant figures when $\gamma=Z$ (fewer than 10 basis functions were needed). For other eigenvalues in all subspaces, up to 40 basis functions were used with varying values of $\gamma$ between 1 and $Z$ to ensure convergence to at least 5 significant figures

The eigenvalues are then summed according to the Pauli principle and added to $\Lambda(\alpha,\beta)$ to give lower bounds to atomic ground states. The best results were obtained for $a = 1$, $b = 0.37$, $\Lambda(\alpha,\beta) = -1$ and these were used to obtain lower bounds to the ground state energies of atoms He to C. These bounds are reported in table 1 where we compare them with: 1) lower bounds obtained neglecting the electron-electron repulsion; 2) best previous lower bounds found in the literature; and 3) accurate upper bounds.

Table 1: We compare our lower bounds with other lower and upper bounds found in the literature.

| $Z = N$ | Repulsionless * | Our results | Best previous lower bound | Upper bound |
|---|---|---|---|---|
| 2 | -4 | -3.48 | -2.9037 [4] | -2.9037 [7] |
| 3 | -10.125 | -8.95 | -7.7953 [5] | -7.4781 [7] |
| 4 | -20 | -17.5 | -17.7 [6] | -14.667 [7] |
| 5 | -34.375 | -29.6 | -30.6 [6] | -24.594 [8] |
| 6 | -54 | -45.9 | -47.6 [6] | -37.773 [8] |

* These are the exact lower bounds formed by adding up the hydrogenic eigenvalues according to the Pauli exclusion principle.

The reason that lower bounds by the effective field method are too low to be satisfactory is easily seen in the proof of Weyl's inequality for the lowest eigenvalue.

$$\lambda_1(A) = \min_{\substack{u \in Dom(A) \\ \|u\|=1}} \langle u|A|u \rangle = \min_{\substack{u \in Dom(A) \\ \|u\|=1}} [\langle u|A_0 + \Phi|u \rangle + \langle u|B - \Phi|u \rangle]$$

$$\geq \min_{\substack{u \in Dom(A) \\ \|u\|=1}} \langle u|A_0 + \Phi|u \rangle + \min_{\substack{u \in Dom(A) \\ \|u\|=1}} \langle u|B - \Phi|u \rangle$$

$$\geq \min_{\substack{u \in Dom(A_0+\Phi) \\ \|u\|=1}} \langle u|A_0 + \Phi|u \rangle + \min_{\substack{u \in Dom(B-\Phi) \\ \|u\|=1}} \langle u|B - \Phi|u \rangle$$

$$= \lambda_1(A_0 + \Phi) + \lambda_1(B\text{-}\Phi) .$$

From this we can see that equality exists only if the lowest eigenvalues of *A*, $A_0+\Phi$, and *B*-$\Phi$ share the same eigenfunction (or more generally, if they share the same function that minimizes the expectation values). Small deviations from equality will result if the eigenfunctions (or minimizing functions) are similar. In all applications to date of the effective field method to atomic problems, the choice of *B*-$\Phi$ contains no differential operator and thus has no eigenfunctions. In these cases one looks at the function which minimizes the expectation value of *B*-$\Phi$. In addition, the operator $A_0+\Phi$ is constrained to contain single-particle operators only. It is thus very unlikely that the minimizing functions of these three operators will be at all similar.

The effective field method is attractive because it reduces the many-particle lower bound problem to several one-particle eigenvalue problems. It does this by restricting the choice of $\Phi$ to a sum of one-particle operators; however, this choice severely limits how similar the operators $A_0 + \Phi$ and *B* - $\Phi$ can be, which in turn limits how close Weyl's inequality deviates from equality. Accuracy is being traded for simplicity and one cannot have both.

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# Appendix I (preprint)

# Ground state multiplicities of atoms and positive ions

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**Abstract:** A procedure is developed to establish the ground state multiplicities for atoms with any number of electrons. The procedure is applied to two- and three-electron systems. The results are that all neutral and positive two- and three-electron atoms have singlet ($S$=0) and doublet ($S$=1/2) ground states, respectively.

## INTRODUCTION

In the effort to bound the ground state energy of the Helium atom as precisely as possible, researchers usually limit themselves to working in the singlet ($S$=0) spin subspace to reduce the size of the calculations. It is widely accepted that the ground states of helium and other isoelectronic atoms (such as $H^-$, $Li^+$, and $Be^{++}$) are singlet states. Support for this comes from experiment [1] and extremely large variational calculations [2]; however, the authors have found no rigorous theoretical support for this. Hylleraas [3] gives a non-rigorous argument using first order perturbation theory. In summary, he remarks "As a general rule the energy of an *ortho* [$S$ = 1] state, hence, is below that of the corresponding *para* [$S$ = 0] state. Nevertheless, the lowest states are *para* [$S$ = 0] states because of the elimination of *ortho* [$S$ = 1] states for equal quantum numbers". Unfortunately, perturbation theory cannot be used to prove anything rigorously unless the perturbation expansion is known to converge. Also, the perturbed part of the wavefunction is typically expanded in an incomplete set of functions, which adds to the non-rigor.

In this note, we present a general method that can be used to determine the ground state multiplicity of any atomic system.

## GENERAL RELATIONS

A rigorous upper bound to the ground state energy, which appears similar to that of first order perturbation theory, can be derived [4]. Let the electronic Hamiltonian be $H = H_0 + H'$, where $H_0$ is the sum of the electronic kinetic energy and nuclear attraction terms and $H'$ contains the interelectronic repulsions. For an atomic system, let

$y_n$ and $l_n$ be the $n$th eigenfunction and eigenvalue of $H_0$ . Then, if $\Lambda_1$ is the lowest eigenvalue of $H$ , we have (by the variational theorem)

$$\Lambda_1 \leq \langle y_n | H | y_n \rangle = \langle y_n | H_0 + H' | y_n \rangle$$
$$= \langle y_n | H_0 | y_n \rangle + \langle y_n | H' | y_n \rangle = l_n + \langle y_n | H' | y_n \rangle \tag{1}$$

This gives an upper bound to $\Lambda_1$.

Now consider a particular spin subspace, with spin quantum number S. Let $^S l_1$ be the lowest eigenvalue of $H_0$ and $^S\Lambda_1$ be the lowest eigenvalue of $H$ in the spin-S subspace. Since the electron repulsion operator is positive definite, we know that

$$^S l_1 < {}^S\Lambda_1 \tag{2}$$

This gives an explicit lower bound to $^S\Lambda_1$.

If we could show that $l_n + \langle y_n | H' | y_n \rangle < {}^S l_1$ we would know that the ground state does not occur is the spin-S subspace, for we would have

$$\Lambda_1 \leq l_n + \langle y_n | H' | y_n \rangle < {}^S l_1 < {}^S\Lambda_1 \tag{3}$$

The eigenstates of the full Hamiltonian need not be known in this analysis. All terms are easily calculable from the exactly known hydrogenic states.

We now investigate the relationships in expression (3) with a general Hamiltonian.

Let **X** be the spatial (spin-free) Hilbert space; let **F** be the full (spatial plus spin) Hilbert space; let **S** be the spin-S subspace of **F**; and let **A** be the antisymmetrized subspace of **S**. For a symmetric spin-free Hamiltonian, $H$, it is well known that the eigenstates in **X** can be used to generate the eigenstates in **A**. However, we must be sure that all the eigenstates in **A** can be generated. To show this, we present for completeness and clarity some simple and previously known results which use the fact that a symmetric Hamiltonian, $H$, and the antisymmetrizer, $A$, commute (i.e. $AH = HA$ ).

**Lemma 1:** Given a symmetric spinless Hamiltonian, $H$, all of its eigenstates in **F** can be generated from its eigenstates in **X**.

**Proof:** Let $\{Q_i\}$ be the complete set of $N$ orthonormal spin eigenfunctions. Let $\{\phi_j\}$ be a countable total orthonormal spatial set composed of the Hamiltonian eigenstates in **X** and any other functions

required for completeness. Any eigenfunction of $H$ in $\mathbf{F}$ can be written as

$$\Psi = \sum_{i=1}^{N} Q_i \sum_{j=1}^{\infty} c_{ij} \boldsymbol{f}_j \, .$$ Given such a function, with eigenvalue $\lambda$, we have

$$H\Psi = H \sum_{i=1}^{N} Q_i \sum_{j=1}^{\infty} c_{ij} \boldsymbol{f}_j = \sum_{i=1}^{N} Q_i H \sum_{j=1}^{\infty} c_{ij} \boldsymbol{f}_j \quad \text{and}$$

$$I\Psi = I \sum_{i=1}^{N} Q_i \sum_{j=1}^{\infty} c_{ij} \boldsymbol{f}_j = \sum_{i=1}^{N} Q_i I \sum_{j=1}^{\infty} c_{ij} \boldsymbol{f}_j$$

Since $H\Psi = \lambda\Psi$, we see that $H\sum_{j=1}^{\infty} c_{ij}\boldsymbol{f}_j = I\sum_{j=1}^{\infty} c_{ij}\boldsymbol{f}_j$ for all $i = 1,..,N$. For this to be true, all the $\boldsymbol{f}_j$ must be degenerate eigenfunctions of $H$ in $\mathbf{X}$ with eigenvalue $\lambda$. Thus $\Psi$ is generated from linear combinations of degenerate spatial functions in $\mathbf{X}$. Since $\Psi$ was an arbitrary eigenfunction in $\mathbf{F}$, we see that all eigenfunctions in $\mathbf{F}$ are generated from eigenfunctions in $\mathbf{X}$. ///

**Lemma 2:** Given a symmetric spinless Hamiltonian, $H$,
   **a)** all of its eigenstates in $\mathbf{S}$ can be generated from its eigenstates in $\mathbf{F}$
   **b)** all of its eigenstates in $\mathbf{A}$ can be generated from its eigenstates in $\mathbf{S}$

**Proof:** The eigenstates in $\mathbf{S}$ must also be eigenstates in $\mathbf{F}$ because $\mathbf{S}$ is a subspace of $\mathbf{F}$. The same argument applies to eigenstates in $\mathbf{A}$. In restricting our problem to certain subspaces we only eliminate solutions outside those subspaces. ///

**Theorem 1:** Given a symmetric spinless Hamiltonian, $H$, all of its eigenstates in $\mathbf{A}$ can be generated from its eigenstates in $\mathbf{X}$.

**Proof:** This results merely from using lemma 2 on lemma 1. We note that all of the eigenstates in $\mathbf{X}$ used to generate an eigenstate in $\mathbf{A}$ by antisymmetrization must have common energy eigenvalues and all the added spin functions must have common spin eigenvalues. ///

**Theorem 2:** For a spin-free Hamiltonian, when eigenstates in $\mathbf{X}$ are used to generate eigenstates in $\mathbf{A}$, the energy eigenvalue, $\lambda$, is the same for both problems.

**Proof:** Using theorem 1, we can write any eigenfunction as linear combinations of degenerate spin eigenfunctions and degenerate spatial eigenfunctions in **X** with eigenvalue $\lambda$. Omitting indices for simplicity and assuming that $A(\sum Q \sum \Phi)$ is normalized, we have

$$
\begin{aligned}
E &= \left\langle A(\textstyle\sum Q \sum \Phi) \middle| H \middle| A(\textstyle\sum Q \sum \Phi) \right\rangle = \left\langle A(\textstyle\sum Q \sum \Phi) \middle| HA(\textstyle\sum Q \sum \Phi) \right\rangle \\
&= \left\langle A(\textstyle\sum Q \sum \Phi) \middle| AH(\textstyle\sum Q \sum \Phi) \right\rangle = \left\langle A(\textstyle\sum Q \sum \Phi) \middle| A(\textstyle\sum Q \sum H\Phi) \right\rangle \\
&= \left\langle A(\textstyle\sum Q \sum \Phi) \middle| A(\textstyle\sum Q \sum l\Phi) \right\rangle = l \left\langle A(\textstyle\sum Q \sum \Phi) \middle| A(\textstyle\sum Q \sum \Phi) \right\rangle \\
&= l
\end{aligned}
$$

Thus the energy eigenvalue is equal to the eigenvalue of any of the degenerate spatial components of the wavefunction. An identical argument shows that the spin eigenvalue is equal to the common spin eigenvalue of the spin components of the wavefunction.                    ///


## TWO-ELECTRON ATOMS

The spatial and spin components of two-electron wavefunctions are separable. Therefore, we can limit our attention to symmetric spatial functions when working in the singlet ($S$=0) subspace (the spin functions are antisymmetric) and antisymmetric spatial functions when working in the triplet ($S$=1) subspace (where the spin functions are symmetric).

We know that $l_1 = -Z^2$ , which is the sum of the eigenvalues of two 1$s$ orbitals (we can ignore the spin part by theorem 2), and $\left\langle y_1 \middle| H' \middle| y_1 \right\rangle = \left\langle 1s1s \middle| H' \middle| 1s1s \right\rangle = 5Z/8$ . Thus

$$
\Lambda_1 \le -Z^2 + 5Z/8
$$

We also know that $H_0$ gives lower bounds to the true eigenvalues of $H_0 + H'$ since $H'$ is positive definite. For the triplet ($S = 1$) subspace, we know that the sum of the eigenvalues of the 1$s$ and 2$s$ orbitals $(-Z^2/2 - Z^2/8)$ is a lower bound to the lowest eigenvalue. If $\Lambda_1 < -Z^2/2 - Z^2/8$, we then have that the lowest eigenvalue in the *whole* Hilbert space is less than all the eigenvalues in the *triplet* subspace, and must therefore belong to the singlet subspace.

We don't know $\Lambda_1$, but we know an upper bound: $\Lambda_1 \le -Z^2 + 5Z/8$. Thus, to show that $\Lambda_1$ is not in the triplet subspace, we must find when

$$^{0}l_{1} = -Z^{2} + 5Z/8 < -Z^{2}/2 - Z^{2}/8 = {^{1}}l_{1}$$

is satisfied. A little manipulation reveals that this is true when $Z > 5/3$. This shows that for $Z \geq 2$, all two-electron atoms have a singlet ground state. For $Z = 1$, Hill proved [5] that there exists only one bound singlet state and that there are no bound triplet states; thus the ground state for H⁻ is a singlet state. Combining Hill's result with ours shows that *all* two-electron atoms have singlet ($S=0$) ground states.

## THREE-ELECTRON ATOMS

For three-electron atoms, there are again only two spin states: the doublet ($S=1/2$) and quartet ($S=3/2$). Unfortunately, the wavefunctions can no longer be factored into products of spatial and spin components. A complete set of orthonormal spin eigenfunctions is [6]:

| | | |
|---|---|---|
| $S = 1/2$ | $1/\sqrt{6}\,(2\alpha\alpha\beta - \alpha\beta\alpha - \beta\alpha\alpha)$ | $1/\sqrt{2}\,(\alpha\beta\alpha - \beta\alpha\alpha)$ |
| | $1/\sqrt{6}\,(2\beta\beta\alpha - \beta\alpha\beta - \alpha\beta\beta)$ | $1/\sqrt{2}\,(\beta\alpha\beta - \alpha\beta\beta)$ |
| $S = 3/2$ | $1/\sqrt{3}\,(\alpha\alpha\beta + \alpha\beta\alpha + \beta\alpha\alpha)$ | $\alpha\alpha\alpha$ |
| | $1/\sqrt{3}\,(\beta\beta\alpha + \beta\alpha\beta + \alpha\beta\beta)$ | $\beta\beta\beta$ |

To find the lowest energy eigenvalue of the repulsionless Hamiltonian in the spin subspaces (for use in equation 3), we must know which one-electron orbitals are used in the wavefunction. By theorem 2, we know that the energy eigenvalue is independent of the spin parts. However, the antisymmetrizer annihilates certain products of spin and spatial functions.

If $a$, $b$, and $c$, denote different orthonormal spatial orbitals, and $Q$, a spin eigenfunction, then in the doublet space A($aaaQ$) vanishes, and both A($aabQ$) and A($abcQ$) are nonzero. In the quartet space, A($aaaQ$) and A($aabQ$) both vanish; only A($abcQ$) survives. Thus the lowest eigenvalue for the doublet subspace, $^{1/2}\lambda_{1} = -Z^{2}/2 - Z^{2}/2 - Z^{2}/8 = -9Z^{2}/8$, comes from the $1s1s2s$ spatial term (or equivalently replace $2s$ with a $2p$ orbital). And the lowest eigenvalue for the quartet subspace, $^{3/2}\lambda_{1} = -Z^{2}/2 - Z^{2}/8 - Z^{2}/8 = -6Z^{2}/8$, comes from the $1s2s2p$ spatial term.

To show when (if ever) equation (3) holds, we work with the function $1s1s2s\boldsymbol{aba}$, which is a solution of the repulsionless Hamiltonian in the doublet subspace, and gives a nonzero function when it is antisymmetrized. In equation (3), we require the integral

$$\langle \boldsymbol{y}_{n} \,|\, H' \,|\, \boldsymbol{y}_{n} \rangle = \langle A(1s1s2s\boldsymbol{aba}) \,|\, 1/r_{12} + 1/r_{13} + 1/r_{23} \,|\, A(1s1s2s\boldsymbol{aba}) \rangle$$

An upper bound will suffice for this. We therefore neglect the exchange terms, and use

$$<1s1s2s/1/r_{12}+1/r_{13}+1/r_{23}/1s1s2s> = Z(5/8 + 17/81 + 17/81) = Z(677/648)$$

Substituting our values into equation (3), we obtain

$$\Lambda_1 \leq {}^{1/2}l_1 + \langle \psi_1 | H' | \psi_1 \rangle = -\frac{9}{8}Z^2 + \frac{677}{648}Z < -\frac{6}{8}Z^2 = {}^{3/2}l_1 < {}^{3/2}\Lambda_1$$

Rearranging, we find that the middle inequality is true when $Z > 677/243$. Thus we can conclude that all three-electron atoms with $Z \geq 3$ have doublet ($S=1/2$) ground states.

## CONCLUSION

This same procedure can be extended to any number of electrons, although the analysis will become tedious very quickly. It is expected that as the number of electrons increases, the generality of the method will suffer. Indeed for the four-electron case, a general proof shows only that atoms with $Z \geq 5$ (i.e. positively charged) have ($S=0$) ground states, and a specific calculation must be done for $Z = 4$ (neutral Beryllium).

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