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CONTENTS

I. ELECTRONIC STRUCTURE THEORY: ATOMS

A. Hydrogenic atoms

Consider the Hamiltonian for the interaction between a nucleus of charge $+Z$ and a single electron (Here we will use ρ for the distance from the origin in spherical polar coordinates. We will then change variables, to be left with r, which is the more usual variable)

$$\begin{aligned} H(r,\theta,\phi) &= -\frac{\hbar^2}{2m_e\rho^2}\nabla^2 - \frac{Ze^2}{4\pi\epsilon_o\rho} \\ &= -\frac{\hbar^2}{2m_e\rho^2}\left[\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) + \frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right] - \frac{Ze^2}{4\pi\epsilon_o\rho} \\ &= -\frac{\hbar^2}{2m_e\rho^2}\left[\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) - \hat{L}^2(\theta,\phi)\right] - \frac{Ze^2}{4\pi\epsilon_o\rho} \qquad (1) \end{aligned}$$

where $\hat{L}^2$ is the operator for the square of the angular momentum of the electron moving around the nucleus. Technically, the mass which appears should be the proton-electron reduced mass

$$\mu = \frac{m_p m_e}{m_p + m_e}$$

but since m_e is ∼2000 times smaller than m_p, $\mu \simeq m_e$.

We can simplify things if we define the distance in terms of the so-called Bohr radius a_0 (the radius of the electron in the Bohr theory of the H atom), namely

$$r = \rho/a_0$$

where

$$a_o = \frac{4\pi\epsilon_o\hbar^2}{m_e e^2}$$

In terms of r the potential becomes

$$V = -\frac{Ze^2}{4\pi\epsilon_o\rho} = \frac{-e^4 m_e Z}{(4\pi\epsilon_o)^2\hbar^2 r}$$

Problem 1 : Use the chain rule

$$\frac{d}{dy} = \frac{dx}{dy}\frac{d}{dx}$$

to show that

$$\frac{\hbar^2}{2m_e}\frac{\partial^2}{\partial\rho^2} = \frac{m_e e^4}{2(4\pi\epsilon_o)^2\hbar^2}\frac{\partial^2}{\partial r^2}$$

Use this result to show that in terms of r, θ and ϕ, the Hamiltonian of Eq. (1) is

$$H(r,\theta,\phi) = \frac{m_e e^4}{(4\pi\epsilon_o)^2\hbar^2}\left\{-\frac{1}{2r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \hat{L}^2(\theta,\phi)\right] - \frac{Z}{r}\right\} \tag{2}$$

The Schrodinger equation for the motion of the electron in a hydrogenic atom is

$$H(\rho,\theta,\phi)\psi(\rho,\theta,\phi) = E\psi(\rho,\theta,\phi)$$

Replacing ρ with r and using Eq. (2), we have

$$\left\{-\frac{1}{2r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \hat{L}^2(\theta,\phi)\right] - Z/r\right\}\psi(r,\theta,\phi = \varepsilon\psi(r,\theta,\phi) \tag{3}$$

where

$$\varepsilon = \frac{(4\pi\epsilon_o)^2\hbar^2}{m_e e^4}E$$

Thus, we see that if we measure the distance in units of a_0 (the atomic unit of distance, called the *bohr*) and the energy in units of $m_e e^4/[(4\pi\epsilon_o)^2\hbar^2]$ (the atomic unit of energy, sometimes called the *Hartree*), we can eliminate all the messy constants from the Schrodinger equation. We have already introduced these atomic units in the first section of Chapter 1. If we multiply Eq. (3) by $2r^2$ and take the right hand side over to the left, we get

$$\left[-\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \hat{L}^2(\theta,\phi) - 2Zr - 2r^2\varepsilon\right]\psi(r,\theta,\phi = 0 \tag{4}$$

which we can write as

$$\left[\hat{H}_r(r) + \hat{L}^2(\theta,\phi)\right]\psi(r,\theta,\phi) = 0 \tag{5}$$

where the definition of $\hat{H}_r(r)$ is obvious from comparison of Eqs. (4) and (5).

Here we have separated the Hamiltonian operator into a term depending only on r and a term depending only on θ and ϕ. In this case, the mathematics of partial differential equations allow us the write the solution as a product of a term depending only on r and a term depending only on θ and ϕ, namely

$$\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$$

Inserting this into Eq. (5), dividing by ψ and simplifying we get

$$\hat{H}(r)\psi(r, \theta, \phi) = -\hat{L}^2(\theta, \phi)\psi(r, \theta, \phi)$$

or

$$Y(\theta, \phi)\hat{H}(r)R(r) = -R(r)\hat{L}^2 Y(\theta, \phi)$$

We can divide by $\psi(r, \theta, \phi) = R(r)Y(\theta, \phi)$, and simplify to get

$$\frac{\hat{H}(r)R(r)}{R(r)} = -\frac{\hat{L}^2 Y(\theta, \phi)}{Y(\theta, \phi}$$

Here, the left-hand side depends only on r while the right-hand side depends only on θ and ϕ. For this equality to be true in general, each side, separately, has to be equal to a constant. Let's call this constant K. Thus, we have

$$-\frac{\hat{L}^2 Y(\theta, \phi)}{Y(\theta, \phi}) = K \tag{6}$$

and

$$\frac{\hat{H}(r)R(r)}{R(r)} = K \tag{7}$$

Equation (6) can we rewritten as the eigenvalue equation

$$\hat{L}^2 Y(\theta, \phi) = -KY(\theta, \phi)$$

which is identical to the Schrodinger equation for the rigid rotor. The solutions must be finite and single valued. In other words

$$Y(\theta + \pi, \phi) = Y(\theta, \phi)$$

and

$$Y(\theta, \phi + 2\pi) = Y(\theta, \phi)$$

To satisfy these boundary conditions, the constant K must equal $-j(j+1)$, where j is a positive semi-definite integer ($j = 0, 1, 2, \ldots$). Here, to avoid confusion of l (el) with the number one, we use j to designate the rotational angular momentum with m its projection.

The solutions are called Spherical Harmonics, $Y_{jm}(\theta, \phi)$; you can find expressions many places. They are eigenfunctions of $\hat{L}^2$ and $\hat{L}_z$, namely (in atomic units)

$$\hat{L}^2 Y_{jm}(\theta, \phi) = j(j+1) Y_{jm}(\theta, \phi)$$

and

$$\hat{L}_z Y_{jm}(\theta, \phi) = m Y_{jm}(\theta, \phi)$$

The spherical harmonics are normalized and orthogonal. In other words, the integral of the product of two spherical harmonics over all angles, weighted by the area element in spherical polar coordinates,

$$dA = \sin\theta \, d\theta \, d\phi$$

is

$$\int\int Y^*_{j'm'}(\theta, \phi) Y_{jm}(\theta, \phi) dA = \delta_{jj'} \delta_{mm'}$$

With the restriction that $K = -j(j+1)$, we can rewrite Eq. (7) as

$$\hat{H}(r) R(r) = j(j+1) R(r)$$

or

$$\left[-\frac{1}{2r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{Z}{r} + \frac{j(j+1)}{2r^2} - \varepsilon \right] R(r) = 0 \tag{8}$$

We can further simplify this equation by defining a new function $G(r)$,

$$R(r) = G(r)/r$$

Problem 2: Show that

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right]R(r)=\frac{1}{r}\frac{\partial^2 G(r)}{\partial r^2}$$

Then show that Eq. (8) reduces to

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial r^2}-\frac{Z}{r}+\frac{j(j+1)}{2r^2}\right]G(r)=\varepsilon G(r) \tag{9}$$

Equation (9) is entirely equivalent to the usual one-dimensional Schrodinger equation, with potential

$$V(r)=-\frac{Z}{r}+\frac{j(j+1)}{2r^2}$$

At large r, the second term, which varies as r^{-2}, goes to zero faster than the first term, which varies only as r^{-1}. Similarly, as $r\to 0$, the 2nd term goes to $+\infty$ faster than the first term goes to $-\infty$. The potential is consequently negative at large r but positive at small r, as shown in Fig. 1.

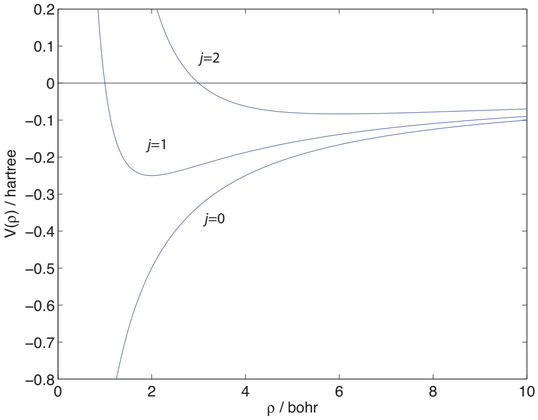

FIG. 1. $V(r)$ for the hydrogen atom ($Z=1$), with $j=0$, 1 and 2.

The solution $G(r)$ has to behave correctly at the origin, and go to zero at infinity. It is possible to show that the limiting behavior at the origin is

$$\lim_{r\to 0} G_j(r) \sim r^{j+1}$$

The radial functions $R(r)$ are tabulated many places. They are real and proportional to Laguerre polynomials, and are indexed in the principal quantum number n, as well as in j (but not m). Here n is restricted to positive integers. Further, for a given n, the allowed values of j are restricted to all positive integer values less than $n-1$. The functions are normalized by integration over all r with the volume element r^2dr, so that

$$\int_0^\infty R_{n',j'}(r)R_{n,l}(r)r^2dr = \int_0^\infty G_{n',j'}(r)G_{n,j}(r)dr = \delta_{n,n'}\delta_{j,j'} \tag{10}$$

The energy, in atomic units, is given by the famous Rydberg formula

$$\varepsilon_n = -\frac{Z^2}{2n^2}$$

Note that the energy is independent of j. For the hydrogen atom all rotational and projection levels with principal quantum number n are degenerate. This is remarkable. Despite the large difference between the $j=0$, $j=1$, and $j=2$ potentials seen in Fig. 1, the energy of the second level in the $j=0$ potential equals exactly the energy of the first level in the $j=1$ potential. Similarly, the energy of the third level in the $j=0$ potential equals exactly the energy of the second level in the $j=1$ potential, and both equal exactly the energy of the first level in the $j=2$ potential.

The other thing to note is that the radial functions $R_{nj}(r)$ have $n-j-1$ *nodes*. [A node is a discrete values of r greater than zero and less than $+\infty$ where $R(r)$ vanishes]. Also, at large r, the behavior of the wave function is given by

$$\lim_{r\to\infty} G(r) \sim r^{n-1}\exp(-rZ/n)$$

.

Problem 3:

The radial functions for the $1s$ and $2p$ states are

$$R_{1s}(r) = N_{1s}\exp(-Zr) \tag{11}$$

$$R_{2p}(r) = N_{2p}\, r \exp(-Zr/2)$$

Use Eq. (10) to show that

$$N_{1s} = 2\zeta^{3/2}$$

Then determine a similar expression for the normalization coefficient N_{2p}. Remember that the normalization relation is given by Eq. (10).

The radial function for the $2s$ state is

$$R_{2s}(r) = N_{2s}(1 + Br)\exp(-Zr/2)$$

Determine the value of N_{2s} and B. In solving this problem you will need the integral

$$\int_0^\infty x^n exp(-\alpha x) dx = \frac{n!}{\alpha^{n+1}}$$

At what value of r does the node in the $2s$ radial function occur?

Then, determine the expectation values of r and $1/r$ in the $1s$, $2s$, and $2p$ states of a one-electron atom with nuclear charge Z. The expectation value of r is an estimate of the size of the one-electron atom.

Finally, suppose you have a hydrogen atom with the electron replaced by a negative muon. What would be the radius of this atom?

B. Other central potential problems

An entirely similar procedure can be used to solve other two-particle problems in which the potential depends only on the distance between the two particles. The Hamiltonian is similar to Eq. (1),

$$H(r,\theta,\phi) = -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) - \hat{L}^2(\theta,\phi)\right] + V(r) \tag{12}$$

where μ is the reduced mass of the two particles $\mu = (m_a m_b)/(m_a+m_b)$. [Equation (8) refers specifically to the hydrogen atom where the mass is equal to unity in atomic units.] The wavefunction is separable into the product of a spherical harmonic and a radial function $R(r)$. This latter can be written as $G(r)/r$, where $G(r)$ satisfies the one-dimensional (ordinary) differential equation:

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2} + V(r) + \frac{\hbar^2 j(j+1)}{2\mu r^2}\right]G(r) = \varepsilon G(r) \tag{13}$$

Problem 4: Consider a spherical box, defined by the potential

$$V(r) = 0,\ r \le a$$

and

$$V(r) = \infty,\ r > a$$

The boundary conditions for the radial wave function $G(r)$ are then that $G(r)$ vanish at $r = a$ and satisfy Eq. (13) with $V(r) = 0$ inside, in other words (in atomic units)

$$\left[-\frac{1}{2\mu}\frac{d^2}{dr^2} + \frac{j(j+1)}{2\mu r^2}\right]G(r) = \varepsilon G(r),\ r \le a \tag{14}$$

By making a variable change $z = (2\mu\varepsilon)^{1/2}r$, use the chain rule

$$\frac{d}{dr} = \frac{dz}{dr}\frac{d}{dz}$$

show that this equation is equivalent to the *Ricatti-Bessel* equation

$$\left[z^2\frac{d^2}{dz^2} + z^2 - n(n+1)\right]w_n(z) = 0$$

Here, we have replaced the integer index j by the integer index n, to avoid confusion later.

The solutions which behave regularly at the origin are

$$w_n(z) = z j_n(z)$$

where $j_n(z)$ is a spherical Bessel function of the first kind (see also section 10.4.7 in the NIST digital library of mathematical functions or the equivalent section in the classic *Handbook of Mathematical Functions* by M. Abramowitz and I. Stegun. Explicit expressions for these functions are, for $n = 0, 1, 2$ (shown in Fig. 2)

$$w_0(z) = \sin z$$

$$w_1(z) = z^{-1} \sin z - \cos z$$

$$w_2(z) = (3z^{-2} - 1) \sin z - 3z^{-1} \cos z$$

In general, in terms of the regular Bessel function $J_n(z)$, we have

$$w_n(z) = \left(\frac{\pi z}{2}\right)^{1/2} J_{n+1/2}(z)$$

The allowed energy levels are those for which $w(z)$ vanishes at $z = (2\mu\varepsilon)^{1/2} r_0$. In other words, $(2\mu\varepsilon)^{1/2} r_0$ must correspond to a root of $w_n(z)$. Determine the first and second roots of $w_0(z)$ and $w_1(z)$ [the lowest two values of z for which $w_0(z)$ and $w_1(z)$ vanish], as well as the first root of $w_2(z)$.

Hint: to work this in Matlab, you first have to define a function, $w_1(x)$, say, using Matlab's anonymous function capability

`w1(x)=@(x) sin(x)/x - cos(x)`

This defines a function w1(x) which is equal to (sin x)/x - cos x. The "@(x)" indicates that you're defining an anonymous function of x which will be defined immediately after the @(x). Then, you need to search for a root of w_1 between, say 0.5π and 1.5π

`fzero(w1,[0.5 1.5]*pi)` *The answer comes back as 4.4934, which is 1.4303π. Alternatively, in Wolfram alpha, you would enter the request "using Newtons method* *solve sin(x)/x - cos(x)=0". The answer comes back as 4.4934. To get the 2nd root, you should enter the request "using Newtons method solve sin(x)/x - cos(x) = 0 starting at x=10" (or whatever you think would be a good initial guess).*

From the values you obtain for the roots of $w_1(x)$, $w_2(x)$ and $w_3(x)$, determine, as a function of the radius of the box r_0, the energy of the lowest two s $(n=0)$ and p $(n=1)$ levels of an electron in a spherical box as well as the energy of the lowest d $(n=2)$ level. What should the radius of the box (in Bohr) be so that the energy of the 1s → 2p transition is equal to that of the H atom?

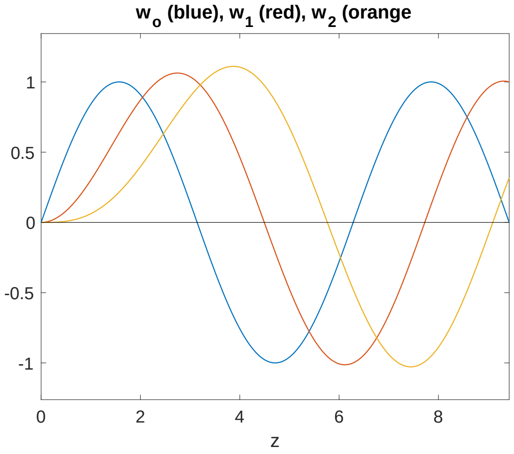

FIG. 2. Ricatti-Bessel functions $w(z)$ for n=0, 1, and 2.

C. Perturbation and simplest variational treatment of the He atom

The Hamiltonian for the motion of the two electrons in the He atom is (in atomic units)

$$H(1,2) = h(1) + h(2) + 1/r_{12} \tag{15}$$

Here, r_{12} is the distance between the two electrons

$$r_{12} = |\vec{r}_1 - \vec{r}_2|$$

and the one-electron Hamiltonian h is the sum of the operator for the kinetic energy of the electron and the attraction of the electron to the nucleus, namely

$$h(1) = -\frac{1}{2}\nabla_1^2 - Z/r_1 \tag{16}$$

and, similarly, for $h(2)$.

In a perturbation theory approach, we can treat the electron repulsion as the perturbation, so that the zeroth order Hamiltonian is

$$H_0 = h(1) + h(2)\,. \tag{17}$$

This Hamiltonian is separable so that the wavefunction can be written as the product of two hydrogenic one-electron functions $\psi_{n,l,m}$ and the total energy is the sum of the hydrogenic energies, namely

$$E_n^{(0)} = -\frac{Z^2}{2}\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right)$$

Here the index n is a collective index for $n_1, l_1, m_1, n_2, l_2, m_2$. In the lowest state, with energy $E_0^{(0)} = -Z^2$, both electrons are described by the hydrogenic $1s$ function

$$1s(r) \equiv R_{1s}(r)Y_{00}(\theta,\phi) = R_{1s}(r)\left(\frac{1}{4\pi}\right)^{1/2} = \left(\frac{Z^3}{\pi}\right)^{1/2}\exp(-Zr)\,. \tag{18}$$

The two-electron wavefunction is

$$\psi_0^{(0)}(1,2) = 1s(1)1s(2) \tag{19}$$

The first-order correction to the energy is just the expectation value of the perturbation, namely, for the ground state

$$\begin{aligned} E_0^{(1)} &= \left\langle \psi_0^{(0)}(1,2) \right| r_{12}^{-1} \left| \psi_0^{(0)}(1,2) \right\rangle \\ &= \iint 1s(1)1s(1)\frac{1}{r_{12}}1s(2)1s(2)dV_1dV_2 \\ &= \left(\frac{Z^3}{\pi}\right)^2 \int_0^\infty r_1^2dr_1 \int_0^\infty r_2^2dr_2 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 e^{-2Zr_1}e^{-2Zr_2}r_{12}^{-1} \end{aligned} \tag{20}$$

This 6-dimensional “two-electron” integral can be evaluated by making use of the expansion

$$\frac{1}{r_{12}} = \sum_{\lambda=0}^{\infty} \frac{r_<^{\lambda}}{r_>^{\lambda+1}} P_\lambda(\cos\theta_{12}) \tag{21}$$

Here $r_<$ and $r_>$ are the smaller and larger of r_1 and r_2, in other words: $r_< = \min(r_1, r_2)$. Also P_λ is a Legendre polynomial and θ_{12} is the angle between $\vec{r}_1$ and $\vec{r}_2$. The definition of the dot product of two vectors implies that

$$\cos\theta_{12} = \vec{r}_1 \cdot \vec{r}_2/(r_1 r_2)$$

Thus, using the projection of $\vec{r}$ into Cartesian coordinates

$$\vec{r} = r(\cos\theta\hat{z} + \sin\theta\cos\phi\hat{x} + \sin\theta\sin\phi\hat{y})\,,$$

we obtain

$$\cos\theta_{12} = \cos\theta_1\cos\theta_2 + \sin\theta_1\sin\theta_2(\cos\phi_1\cos\phi_2 + \sin\phi_1\sin\phi_2)$$

Since the s functions are spherical, only the λ=0 term in Eq. (21) will give a non-vanishing result, so when evaluating Eq. (21), you can use

$$\frac{1}{r_{12}} = \frac{1}{r_>} \tag{22}$$

Problem 5: Show that the $\lambda = 1$ term in Eq. (21) makes a vanishing contribution to $E_0^{(1)}$ (Eq. 21).

Thus, schematically,

$$\iint f(r_1)\frac{1}{r_{12}}g(r_2)d\tau_1 d\tau_2 = 16\pi^2\left[\int_0^{\infty} f(r_1)r_1 dr_1 \int_0^{r_1} g(r_2)r_2^2 dr_2 + \int_0^{\infty} g(r_2)r_2 dr_2 \int_0^{r_2} f(r_1)r_1^2 dr_1\right] \tag{23}$$

In the first integral on the right-hand-side, r_2 is always less than r_1 so that $\frac{1}{r_>} = 1/r_1$. In the second integral, r_1 is always less than r_2 so that $\frac{1}{r_>} = \frac{1}{r_2}$. Figure 3 depicts the domain of integration. Both r_1 and r_2 can range over all positive values. The diagonal line corresponds to $r_1 = r_2$. In the red shaded region r_1 is greater than r_2. This region corresponds to the first double integral in Eq. (23).

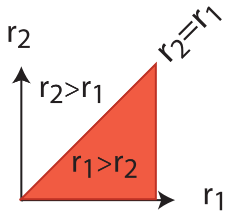

FIG. 3. Illustration of the range of integration in Eq. (23)

Problem 6: Show that

$$[1s^2|1s^2] \equiv [1s1s|1s1s] = \int\int 1s(1)^2 \frac{1}{r_{12}} 1s(2)^2 dV_1 dV_2 = \frac{5Z}{8} \tag{24}$$

With the result of this problem, we see that the energy of the ground $(1s^2)$ state of the two-electron ion with nuclear charge Z is predicted to be

$$E_0^{(0)} + E_0^{(1)} = -Z^2 + \frac{5Z}{8}$$

For He this is –2.75 hartree. The true energy of He can be determined by adding the binding energies of the two electrons. The binding energy of the first electron is just the energy of $1s$ state of He^+, namely –2. The binding energy of the second electron is just the negative of the ionization potential of the He atom. To get this, go to the the NIST tables of electron energy levels of the atoms and positive ions. Enter `He I` (that's the designator for the He atom, the `I` means the neutral atom. The designator `II` would mean the single-ionized atom (the positive ion), `III` would mean the doubly-ionized atom, and so forth). When the window returns data, scroll down until you find `He II (2S1/2) Limit 198 310.669`. This is the ionization potential of He. Converting from wave numbers to

Hartree (dividing by 201474.6) shows that the ionization potential is 0.90357 Hartree. Thus, the total electronic energy of He is $-2+(-0.90357) = -2.90357$ Hartree. The perturbation theory estimate of –2.75 is quite poor.

To zeroth-order the wavefunction for He [Eq. (19] is a product of one-electron hydrogenic orbitals. Approximating a multi-electron wavefunction as a product of one-electron functions is how we will describe wavefunctions of all many-electron atoms and, eventually, molecules. For He, as we have seen, the zeroth-order choice for these one-electron functions are $1s$ functions with exponential factors $(-Zr)$ which depend on the nuclear charge. We can improve this, quite easily, by replacing the nuclear charge (Z) by a variable constant ζ. Because each electron screens the other electron to some extent, we anticipate that ζ will be less than Z. In other words, we can define a generalized hydrogenic $1s$ orbital

$$1s_\zeta = \left(\frac{\zeta^3}{\pi}\right)^{1/2} \exp(-\zeta r) \tag{25}$$

where ζ is a variable screening constant. In this variable-ζ approximation the He wavefunction is, instead of Eq. (19,

$$\psi_\zeta(1,2) = 1s_\zeta(1)1z_\zeta(2) \tag{26}$$

We will then calculate the variational energy

$$E_{var} = \langle\psi(1,2)|\hat{H}|\psi(1,2)\rangle/\langle\psi(1,2)|\psi(1,2)\rangle = 2\,\langle 1s_\zeta|\,h\,|1s_\zeta\rangle + [1s_\zeta^2|1s_\zeta^2]$$

which will be a function of ζ. By minimizing this expression with respect to varying ζ, we can obtain the best variational estimate of the energy of the two electrons in He, subject to the constraint that the wavefunction is adequately described by the product form of Eq. (26).

Problem 7 Show that $\langle 1s_\zeta|\,h\,|1s_\zeta\rangle = -Z\zeta + \zeta^2/2$

Problem 8: Use the results of problems 6 and 7 to determine an expression in terms of Z and ζ for the variational energy of the He atom. Then minimize this to determine the optimal screening coefficient ζ and the best variational energy.

Problem 9: Consider two $1s$ functions i and j, given by Eq. (25), where $1s_i$ has the screening constant ζ and $1s_j$ has the screening constant ζ'. Determine expressions for the one electron integrals $\langle i|j\rangle$ (overlap), $\langle i| -\frac{1}{2}\nabla^2|j\rangle$ (kinetic energy), and $\langle i| -1/r|j\rangle$ (nuclear-electronic attraction energy). The results will be explicit functions of ζ and ζ'. Also, determine an expression for the coulomb and exchange two-electron integrals.

$$[1s^2|1s'^2] \equiv [1s1s|1s'1s'] = \int\int 1s(1)^2\frac{1}{r_{12}}1s'(2)^2 dV_1 dV_2$$

$$[1s1s'|1s'1s] = \int\int 1s(1)1s'(1)\frac{1}{r_{12}}1s'(2)1s(2) dV_1 dV_2$$

In every case, the results will be a function of both ζ and ζ'. To check your work, Table I gives values of the desired integrals for $\zeta = 1$ and $\zeta' = 3$.

TABLE I. One- and two-electron integrals involving two $1s$ functions: $1s$ with screening constant $\zeta = 1$ and $1s'$ with screening constant $\zeta' = 3$.

integral	value (Hartree)
$\langle 1s\|1s'\rangle$	0.64952
$\langle 1s\| -\frac{1}{2}\nabla^2\|1s'\rangle$	0.94728
$\langle 1s\| -1/r\|1s'\rangle$	–1.2990
$[1s^2\|1s'^2]$	0.89062
$[1s1s'\|1s'1s]$	0.52734

D. Basis set solution of the Hartree equation for the He atom

The choice of the wavefunction for the two-electron He atom which underlies the preceding section is a product of one-electron functions. This is guided by the separation of the Hamiltonian in Eq. (17) in which the zeroth-order Hamiltonian is a sum of identical one-electron terms. The best product wavefunction of this type is given by the Hartree approximation, in which each of the two He 1s electrons moves in the field of the nuclear attraction and in the averaged field of the repulsion with the other electron. Consequently, in the so-called Hartree (or Hartree-Fock [1]) approximation the Schrodinger equation for the 1s electron is the following one-electron, three-dimensional integro-differential equation

$$\hat{H}_{\mathrm{HF}}\phi(r_1) = \left[-\tfrac{1}{2}\nabla_1^2 - \frac{2}{r_1} + \int \frac{\phi^2(r_2)}{r_{12}} d\tau_2\right]\phi(r_1) = \varepsilon_{\mathrm{HF}}\phi(r_1) \tag{27}$$

Since the solution appears under the integral sign, it is most straightforward to solve Eq. (27) iteratively. One guesses a solution, $\phi^{(0)}(r_1)$, which then defines the so-called "mean-field" potential, which we designate V_{ee},

$$V_{ee}(r_1) = \int \frac{|\phi(r_2)|^2}{r_{12}} d\tau_2\,, \tag{28}$$

We then solve the Hartree Schroedinger equation [Eq. (27)] for $\phi^{(1)}(r_1)$, with which we determine a new mean-field potential, and then new value of $\varepsilon_{\mathrm{HF}}$ and so on until convergence is reached, at which point the calculated energy $\varepsilon_{\mathrm{HF}}$ at iteration $n+1$ has not changed significantly from its previous value. The convergence of this iterative process is called "self-consistency", and the overall method: "self-consistent-field" (SCF).

Although for atoms it is possible to do this all numerically, for molecules the only practical method is by expansion of the solution in a basis set. To illustrate this, for simplicity suppose we expand the Hartree-Fock orbital in just two basis functions

$$\phi^{(n)}(r) = c_1^{(n)}\chi_1(r) + c_2^{(n)}\chi_2(r) \tag{29}$$

Here the superscript n designates the n^{th} iteration. From Eqs. (28) and (29), we see that after the n^{th} iteration the mean field potential arising from the repulsion of electron 1 with the averaged position of electron 2 is

$$V_{ee}(r_1) = \int \frac{|\phi(r_2)|^2}{r_{12}} d\tau_2 = \sum_{k,l} c_k^{(n)} c_l^{(n)} \int \chi_k^*(r_2)\frac{1}{r_{12}}\chi_l(r_2) d\tau_2 \tag{30}$$

Here, for simplicity, we will assume that the expansion coefficients are real.

At the $n+1^{th}$ iteration, as in any linear variational method, we obtain the expansion coefficients $c_i^{(n+1)}$ by diagonalizing the matrix of $\hat{H}_{\rm HF}$ in the 2×2 basis of $\{\chi_1, \chi_2\}$. *Note that the basis functions don't change during the iterative process; only the expansion coefficients* c_i. Schematically, the matrix elements of $\hat{H}_{\rm HF}$ are sums of matrix elements of the one-electron Hamiltonian $\hat{h}(1) = -\frac{1}{2}\nabla^2 - 2/r$ and of the mean-field repulsion $V_{ee}(1)$, so that

$$\langle\chi_i|\,\hat{H}_{\rm HF}\,|\chi_j\rangle = -\frac{1}{2}\,\langle\chi_i|\,\nabla^2\,|\chi_j\rangle - \langle\chi_i|\,\frac{2}{r}\,|\chi_j\rangle - \frac{1}{2}\,\langle\chi_i|\,V_{ee}\,|\chi_j\rangle \tag{31}$$

The matrix elements of V_{ee} are

$$(V_{ee})_{ij} = \sum_{k,l} c_k^{(n)*} c_l^{(n)} \int \chi_i^*(r_1)\chi_k^*(r_2)\frac{1}{r_{12}}\chi_j(r_1)\chi_l(r_2)d\tau_2 d\tau_1 \tag{32}$$

We use the compact notation for these so-called two-electron integrals that we have already introduced in Eq. (24) and in Problem 9, namely

$$[ij|kl] = \int \chi_i^*(r_1)\chi_k^*(r_2)\frac{1}{r_{12}}\chi_j(r_1)\chi_l(r_2)d\tau_2 d\tau_1 = \int \chi_i^*(r_1)\chi_j^*(r_1)\frac{1}{r_{12}}\chi_k(r_2)\chi_l(r_2)d\tau_2 d\tau_1 \tag{33}$$

In terms of this notation, Eq. (32) becomes

$$(V_{ee})_{ij} = \sum_{k,l} c_k^{(n)*} c_l^{(n)} [ij|kl] \tag{34}$$

Note that $[ij|kl]$ defines a square matrix of order $N^2 \times N^2 = N^4$. We will designate this matrix as $(h_{12})_{kl}^{ij}$ with the understanding that each ij^{th} element is a 2×2 matrix (two possible values of k and two possible values of l). Let $\mathbf{c}^n$ define a column vector of length 2. Then

$$(V_{ee})_{ij} = \mathbf{c}^{(n)\,\dagger}(h_{12})_{kl}^{ij}\,\mathbf{c}^{(n)}\,, \tag{35}$$

where the superscript † denotes the Hermitian adjoint (that is, a row vector with elements that are the complex conjugates of the column vector $\mathbf{c}^(n)$).

A standard procedure is to use so-called Slater (hydrogenic) functions

$$g_i = N_i \exp(-\zeta_i r) \tag{36}$$

as the basis functions $\{\chi_1,\, \chi_2\}$. Because these functions are not orthogonal, we will need to determine the overlap matrix S with elements $S_{ij} \equiv \langle \chi_i | \chi_j \rangle$, and then use one of the methods described in Subsection D of Chapter 1 to determine the variational energy in this non-orthogonal basis.

Thus, the iterative procedure consists of

(a) Determination of the $N \times N$ matrix of the one-electron Hamiltonian $\hat{h}$ and of the overlap.

(b) Determination of the $N^2 \times N^2$ matrix of two-electron integrals $[ij|kl]$ (many of these will be the same by symmetry; see below).

(c) An initial choice of the $\mathbf{c}^{(0)}$ vector.

(d) Determination of the $N \times N$ matrix of the mean-field repulsion from Eq. (35). (e) Diagonalization of the $N \times N$ matrix of the Hartree Hamiltonian ($\hat{H}_{\text{HF}}$) to determine the new coefficient vector $\mathbf{c}^{(1)}$ and the new Hartree energy $\varepsilon_{\text{HF}}^{(1)}$

(f) Iteration of steps (d) and (e) until self-consistency is reached, at which point $\mathbf{c}^{(n+1)} = c^{(n)}$ and $\varepsilon_{\text{HF}}^{(n+1)} = \varepsilon_{\text{HF}}^{(n)}$. Usually, one choses an energy cutoff criterion:

$$\left| \varepsilon_{\text{HF}}^{(n+1)} - \varepsilon_{\text{HF}}^{(n)} \right| \leq \epsilon \tag{37}$$

where $\epsilon = 10^{-8}$ hartree.

When self-consistency is reached, from Eq. (27) one sees that

$$\varepsilon_{\text{HF}}^{(n)} = \left\langle \phi^{(n)} \middle| \hat{H}_{\text{HF}} \middle| \phi^{(n)} \right\rangle = \left\langle \phi^{(n)} \left| h \right| \phi^{(n)} \right\rangle + \left[\phi^{(n)} \phi^{(n)} | \phi^{(n)} \phi^{(n)} \right] \tag{38}$$

In other words, the Hartree-Fock energy is the one-electron energy of the electron in orbital $\phi^{(n)}$ plus the average repulsion energy of this electron with the other electron. Note, then that twice the Hartree-Fock energy is equal to twice the one-electron energy plus *twice* the two-electron repulsion energy.

In the Hartree approximation the He wavefunction is the product of the one-electron functions which are the iterated solutions to Eq. (27). We have

$$\psi_{\text{HF}}^{(n)}(1,2) = \phi_{\text{HF}}^{(n)}(1) \phi_{\text{HF}}^{(n)}(2) \tag{39}$$

Thus, the total energy of the He atom, in the Hartree-Fock approximation is

$$E_{\text{He}} = 2\varepsilon_{\text{HF}} - \left[\phi^{(n)} \phi^{(n)} | \phi^{(n)} \phi^{(n)} \right] . \tag{40}$$

This result is important: The variational estimate of the total energy of the atom in the Hartree-Fock approximation is n̲ot equal to the sum of the Hartree-Fock orbital energies.

1. *Symmetry of two-electron integrals*

For two basis functions χ_1 and χ_2, there are only 6 distinct matrix elements in the 4×4 matrix of two-electron integrals. If we use the simplified notation $1 \equiv \chi_1$ and $2 \equiv \chi_2$, these distinct matrix elements arer1 $[11|11]$, $[22|22]$, and

$$\begin{aligned} [11|22] &= [22|11] \\ [11|12] = [11|21] = [12|11] &= [21|11] \\ [12|12] = [21|21] = [12|21] &= [21|12] \\ [12|22] = [21|22] = [22|12] &= [22|21] \end{aligned}$$

Table II shows the convergence of this iterative Hartree-Fock procedure, with two basis functions with $\zeta_1 = 1$ and $\zeta_2 = 3$. In this table, C_1 and C_2 are the expansion coefficients in Eq. (29). The convergence is rapid. Note that twice the Hartree-Fock energy $\varepsilon_{\rm HF}$ is NOT equal to the electronic energy of the atom. By varying ζ_1 and ζ_2, you can obtain an even better estimate, as shown in the last line of the table.

TABLE II. Convergence of double-zeta[a] Hartree approximation to the $1s^2$ state of the He atom.

n	ε_n [b]	C_1	C_2	E_{He}
1	–1.1278	0.6462	0.4512	–3.0066
2	–0.8923	0.7483	0.3363	–2.7192
3	–0.9536	0.7203	0.3689	–2.7988
4	–0.9361	0.7282	0.3598	–2.7764
5	–0.9410	0.7260	0.3623	–2.7827
6	–0.9396	0.7266	0.3616	–2.7809
7	–0.9400	0.7264	0.3618	–2.7814
8	–0.9399	0.7265	0.3618	–2.7813
8[c]	–0.9179	0.8416	0.1829	–2.8617

[a] $\zeta_1 = 1$ and $\zeta_2 = 3$.

[b] Energies in Hartree.

[c] $\zeta_1 = 1.452$ and $\zeta_2 = 2.900$.

The best single-exponential ($\zeta = 1.6875$) and Hartree descriptions of the behavior of the $1s$ electron in the He atom are remarkably similar. In Fig. 4 we compare the probability $\rho(r)$ of finding the $1s$ electron at a distance r from the He nucleus

$$\rho(r) = 1s(r)^2 r^2$$

predicted by the Hartree and single-exponential orbitals.

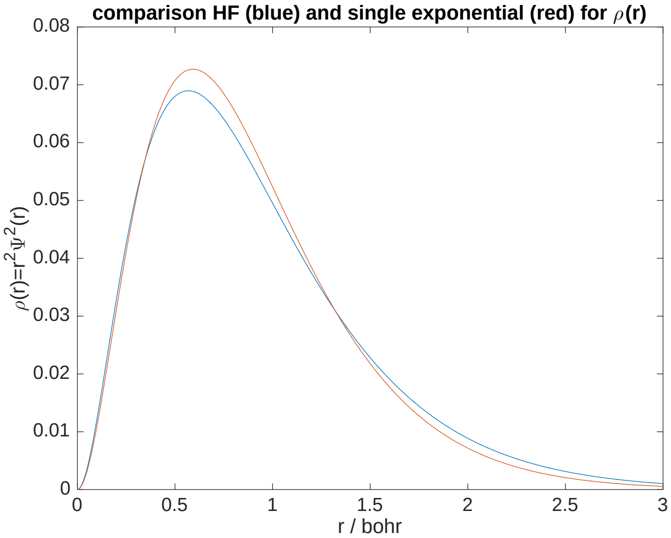

FIG. 4. Illustration of $\rho_{1s}(r)$ for Hartree-Fock (blue) and single-exponential (red: $\zeta = 1.6875$).

We see that the HF density is slightly more delocalized, and hence leads to a slightly lower of the electronic repulsion. From Eq. (24) we calculate that the average repulsion predicted by the single-exponential description is $[1s^2|1s^2]_{\zeta=1.6875} = 1.0547$ H. From Eq. (38) and the last row in Table II we see that $[1s^2|1s^2]_{\rm HF} = 1.0259$ H, slightly lower.

E. Configuration Interaction

Expansion of the solution to the Hartree equation [Eq. (27)] in a basis results, by the variational principle, in an upper bound to the exact Hartree-Fock energy. Often the size of the basis is characterized by the number of Slater functions [Eq. (36)] which are included, with the notation "double-zeta" (dz) for two functions, "triple-zeta" (tz) for three functions, etc.

As we mentioned earlier, the true energy of He is –2.90357 Hartree. This is 0.042 Hartree lower than the Hartree-Fock limit. The reason for this significant error is that in the Hartree-Fock approximation each electron moves in the average field due to the other electron and the nucleus. Instantaneously, each electron avoids the other in a more complicated fashion. It is this instantaneous correlation between the positions of the two electrons which is neglected in the Hartree-Fock approximation. The correction to the energy is called the "correlation energy".

$$E_{corr} = E_{\mathrm{HF}} - E_{exact}$$

This is usually on the order of 1 eV (0.037 Hartree) for each pair of electrons. Table III gives the Hartree-Fock and exact energies of the two-electron ions from H^- up to C^{4+}.

TABLE III. The Hartree-Fock and exact energies[a] of the two-electron ions with nuclear charge Z.

Atom	Z	E_{HF}	E_{exact}
H^-	1	–0.487294	–0.527736
He	2	–2.861677	–2.907325
Li^+	3	–7.236411	–7.279723
Be^{2+}	4	–13.6113000	–13.655582
B^{3+}	5	–21.9862332	–22.031727
C^{4+}	6	–32.3611910	–32.409062

[a] Energies in Hartree units.

Problem 10: From the energies listed in Tab. III answer the following questions:

(a) In the Hartree-Fock approximation would you predict the H^- ion be stable? In other words, will H^- be at a lower energy than H and a free e?

(b) Calculate and plot the correlation energies of the two-electron ions from H^- up to C^{4+}.

(c) Would you expect the correlation energy to increase or decrease with Z? Why?

Recovery of the correlation energy can be achieved only by expanding the variational wavefunction beyond the Hartree-Fock approximation, namely (for He)

$$\Psi(1,2) = \phi_{\rm HF}(1)\phi_{\rm HF}(2) + \sum_{n=1}^{\infty} C_n^{(1)} \phi_{\rm HF}(1)\psi_n(2) + \sum_{n,m=1}^{\infty} C_{nm}^{(2)} \psi_n(1)\psi_m(2)$$

Here $\{\psi_m\}$ is a set of one-electron functions that are orthogonal to the Hartree-Fock 1s ($\phi_{\rm HF}$) orbital. The first summation includes all one-electron (single) excitations out of the Hartree-Fock wavefunction, while the second summation includes all two-electron (double) excitations. To include the exchange symmetry of the electrons, this expansion should be written as

$$\begin{aligned}\Psi(1,2) = \phi_{\rm HF}(1)\phi_{\rm HF}(2) &+ \sum_{n=1}^{\infty} D_n^{(1)} [\phi_{\rm HF}(1)\psi_n(2) + \phi_{\rm HF}(2)\psi_n(1)] \\ &+ \sum_{n,m=1}^{\infty} D_{nm}^{(2)} \frac{1}{1+\delta_{nm}} [\psi_n(1)\psi_m(2) + \psi_n(2)\psi_m(1)] \qquad (41)\end{aligned}$$

The matrix of the Hamiltonian is then constructed in the large basis of singly and doubly excited states, then diagonalized. This technique is called "configuration-interaction", or, CI. In practice, the number of states gets rapidly very large.

For example, suppose you are using a double-zeta s orbital basis. On linear combination is the 1s Hartree-Fock orbital. The second (orthogonal) combination, call it ϕ_2, defines the sole excited (or "virtual") orbital. There is then one singly-excited state $\phi_{\rm HF}\phi_2$ and one doubly-excited state ϕ_2^2. So the CI consists of 3 states. If you use a triple-zeta s orbital basis, then there are two virtual s orbitals. There are two singly-excited states and three doubly-excited states.

If all the virtual orbitals are limited to s functions, then the CI energy is called the "s-limit". One can add p, d, etc functions to the basis, which will all be orthogonal to $\phi_{\rm HF}$. The CI energy is then called the sp-limit, the spd-limit, etc. Table IV shows the convergence of the calculated energy of He as the size of the CI is increased. Eventually, we do get close to the three energy, but the convergence is slow. The number of states and the number of two-electron integrals goes up very dramatically. Thus the calculations rapidly become more difficult while the differential improvement of the calculated energy becomes smaller and smaller.

For a system with more than two electrons, the summation extends over triple, quadruple,

TABLE IV. Convergence of calculated CI energies (Hartree) for the $1s^2$ state of the He atom.

basis	limit	E_{CI}	Δ_E [a]	configurations	two-electron integrals
v5z	Hartree-Fock	-2.86162	4.2×10^{-2}	1	
v5z	*s*-limit	–2.87891	2.5×10^{-2}	15	120
v5z	*sp*-limit	–2.90036	3.2×10^{-3}	45	2535
v5z	*spd*-limit	–2.90255	1.0×10^{-3}	114	21726
v5z	*spdf*-limit	–2.90304	5.3×10^{-4}	195	82977
v5z	*spdfg*-limit	–2.90315	4.2×10^{-4}	261	163437
v6z	*spdf*-limit	–2.90339	1.8×10^{-4}	522	701058
exact [b]		–2.90357			

[a] $E_{calc} - E_{exact}$.

[b] Sum of first and second ionization energies.

and higher-order excitations. In practice, it is very difficult to carry out a full CI calculation including all triple or higher-order excitations. Triple excitations can, however, be included perturbatively. Table V compares the calculated energies for the Be atom with the exact value. The correlation energy is 2.56 eV ($E_{\mathrm{HF}} - E_{exact}$). Of this 82% is recovered by a CI calculation including all single- and double-excitations, and 93% is recovered by the calculation in which triple excitations are included perturbatively. Still, the remaining ≈ 7% of the correlation energy, 0.2 eV, is due to higher-order excitations, which can be included only in extremely computer-intensive calculations. To illustrate this: the HF, CI, and CCSD(T) calculations in Table V took a few minutes on my laptop. But, the FCI calculations took a few *hours*. Note that even when a complete (full) CI calculation is done, the energy lies $\approx 1.9\times10^{-3}$ H above the experimentally-determined value. This error is due to the incompleteness of the basis set used to describe the one-electron orbitals. In principle, any CI calculation is *systematically improvable*, in the sense that you can always go to one more order: including all excitations up to order N, and then all excitations to order $N+1$, and so forth, the way to what is called a *full* CI, in which all single-, double-, triple-, quadruple-, up to $\mathcal{N}$-excitations (where $\mathcal{N}$ is the number of electrons in the atom or molecule). Of course, this may be impossible to achieve in practice.

TABLE V. Convergence of calculated $spdfgh(l = 0 - 5)$-limit[a] energies (Hartree) for the $1s^22s^2$ state of the Be atom.

basis	calculation	$E_{\rm CI}$	Δ_E [b]
v5z	Hartree-Fock	–14.573012	$9.54{\times}10^{-2}$
v5z	CI-SD	–14.662429	$6.01{\times}10^{-3}$
v5z	CC-SD(T)[c]	–14.666506	$1.93{\times}10^{-3}$
v5z	FCI[d]	–14.666538	$1.90{\times}10^{-3}$
exact [e]		–14.668444	

[a] Correlation-consistent, core-valence quintuple zeta basis (pcv5z). 145 total basis functions

[b] $E_{calc} - E_{exact}$.

[c] Coupled-cluster calculation with perturbative inclusion of triple excitations.

[d] Full CI (single+double+triple+quadruple excitations included.

[e] Sum of ionization energies.

F. Cusp condition

The slow convergence of the CI expansion is due to the so-called Kato cusp condition [see C. R. Myers, C. J. Umrigagr, J. P. Sethna, and J. D. Morgan II, Phys. Rev. A **44** 5537 (1991)]. When two particles, of charges q_1 and q_2, and masses m_1 and m_2, approach one another, the slope of the wavefunction is

$$\lim_{r_{12}\to 0} \frac{\partial \Psi}{\partial r_{12}} = \mu_{12} q_1 q_2 \Psi(r_{12}=0) \tag{42}$$

Here, μ_{12} is the reduced mass and r_{12} is the distance between the two particles.

An example of this is the the wavefunction on the position of the electron as it approaches the nucleus. Here, in atomic units, $\mu_{12} \approx 1$, $q_1 = Z$, and $q_2 = -1$, so that $\partial\Psi/\partial r_{12} \to -Z\Psi(0)$. As an example, consider the $1s$ orbital of a hydrogenic atom

$$\phi_{1s} = R_{1s}(r)Y_{00}(\theta,\phi) = (Z^3/\pi)^{1/2}\exp(-Zr)$$

. Here r, the distance between the electron and the nucleus, is just the coordinate r_{12} which appears in Eq. (42). By differentiation, you can show that the cusp condition [Eq. (42)] is exactly satisified. The cusp in the $1s$ orbital (the first derivative with respect to r) at the origin is positive.

Similarly, when two electrons approach one another, $\mu_{12} = 1/2$, $q_1 = q_2 = 1$ so that

$\partial\Psi/\partial r_{12} \to +\frac{1}{2}\Psi(0)$. This corresponds to a negative (downward oriented) cusp at $r_{12} = 0$. As shown in Eq. (41), we are trying to approximate the two-electron wavefunction as a sum of symmetric products of one-electron functions ("orbitals"). It is easy to show from Eq. (41) (and seen in Fig. 5) that for a product of one-electron functions $\lim_{r_{12}\to 0} \partial\Psi/\partial r_{12} = 0$ which is incorrect. So we are trying to approximate a cusp by a sum of functions that are cuspless.

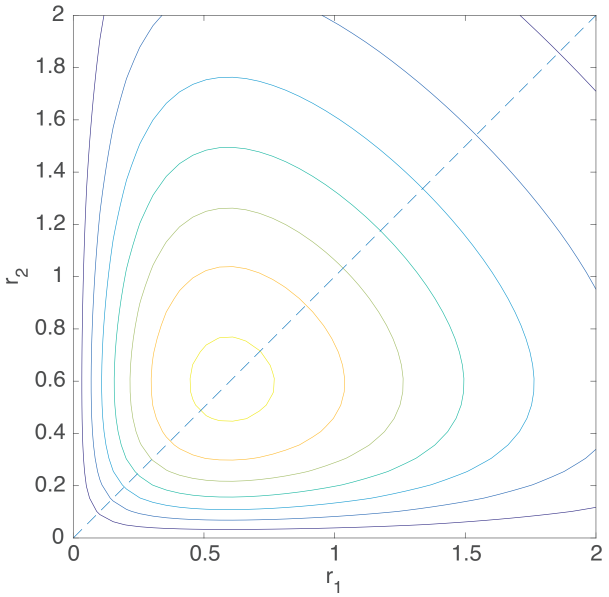

FIG. 5. The Hartree-Fock wavefunction for He is given by Eq. (39)]. Since the 1s function is peaked sharply at $r = 0$ (the electron-nucleus cusp), we have here plotted $r_1 r_2 \psi_{\mathrm{HF}}(r_1, r_2)$. The dashed line corresponds to $r_{12} = 0$. The derivative of the wavefunction with respect to changing r_{12} corresponds to the slope of curves which are perpendicular to this line. . Because the wavefunction is symmetric with respect to interchange ($r_1 \leftrightarrow r_2$), the derivative $\partial\psi/\partial r_{12}$ of this product of one-electron functions vanishes everywhere along the line $r_{12} = 0$.

This can be done, but convergence is slow.

Explicit inclusion of a dependence on r_{ij} in the variational wavefunction can accelerate this convergence. This is the basis of the so-called "explicitly correlated" (R_{12}/F_{12}) methods [L. Kong, F. A. Bischoff, and E. F. Valeev, Chem. Rev. **112** 75, 2012, dx.doi.org/10.1021/cr200204r] which have significantly increased the speed of calculations of electronic energy.

G. Spin states of two-electron systems

In the discussion so far, we have ignored the spin of the electron. The electronic Hamiltonian [Eq. (15)] does not include the spin. Thus, a complete wavefunction including the spin can be written by multiplying a spatial wavefunction of the form $1s(1)1s(2)$ by a component describing the spin of the electrons, namely

$$\Psi(1,2) = 1s(1)1s(2)\,|S(1,2)\rangle\,. \tag{43}$$

Here, the function "$1s(r)$" could designate either the single-exponential of Eq. (25) or a more general one-electron orbital, of spherical (s) symmetry, such as that defined by Eq. (29). This could be the Hartree-Fock $1s$ orbital defined by Eq. (27). Each electron has a spin of 1/2. The spin wavefunction of the electron can be written as $|sm_s\rangle$, where the projection quantum number is $m_s = \pm 1/2$. The spin wavefunction for two electrons can be obtained by vector coupling the spin-wavefunction of each electron.

In quantum mechanics two angular momenta $\vec{j}_1$ and $\vec{j}_2$ can be coupled to form a state of angular momentum j, with $|j_1 - j_2| \leq j \leq j_1 + j_2$. Thus, the total spin for the two-electron system can be either $S = 0$ or $S = 1$. The projection quantum numbers M_S can be only 0 for $S = 0$, but $-1, 0, +1$ for $S = 1$. Since the total projection quantum number is the sum of the projection quantum numbers for each of the two electrons, the wavefunction for $S = 1, M_S = 1$ must be (to within an arbitrary phase)

$$|S = 1, M_S = 1\rangle = |s_1 = 1/2, m_{s_1} = 1/2\rangle|s_2 = 1/2, m_{s_2} = 1/2\rangle$$

To simplify the notation, we write this as

$$|11\rangle = |\tfrac{1}{2}\tfrac{1}{2}\rangle$$

Here we have suppressed the values of s_1 and s_2, which are always 1/2, and designated the so-called "uncoupled" state, in which the m_s quantum numbers are specified for each electron, with the general notation $|m_{s_1}m_{s_2}\rangle$.

Now, the wavefunction for the coupled state with $S = 1, M_S = 0$ can be obtained by the general angular momentum lowering operator. This is

$$j_-|jm_j\rangle = [j(j+1) - m(m-1)]^{1/2}|j, m-1\rangle$$

or, in the particular case where $S = 1$

$$S_{-}|11\rangle = [1 \times 2 - 1 \times 0]^{1/2}|10\rangle = 2^{1/2}|10>$$

or, reversing the order

$$|10\rangle = 2^{-1/2}|11\rangle$$

The lowering operator for the total spin is the sum of the lowering operators for each individual spin

$$S_{-} = s_{1-} + s_{2-}\ ,$$

where the effect of s_{1-} on the spin wavefunction for electron 1 is

$$s_{1-}|\tfrac{1}{2}\rangle = [\tfrac{1}{2} \times \tfrac{3}{2} - \tfrac{1}{2}(\tfrac{-1}{2})]^{1/2}|\tfrac{-1}{2}\rangle = |\tfrac{-1}{2}\rangle$$

Problem 11: Use the uncoupled and coupled lowering operators to show that (the coupled wavefunction is on the left and the uncoupled wavefunction is on the right

$$|10\rangle = 2^{-1/2}(|\tfrac{1}{2}, \tfrac{-1}{2}\rangle + |\tfrac{-1}{2}, \tfrac{1}{2}\rangle) \tag{44}$$

and

$$|1-1\rangle = |\tfrac{-1}{2}, \tfrac{-1}{2}\rangle$$

Now, the wavefunction for the sole state with $S = 0$ and $M_S = 0$ must be a linear combination of the uncoupled wavefunctions $|m_{s1} = \pm 1/2, m_{s2} = \mp 1/2\rangle$. In other words

$$|00\rangle = C_{1,-1}|\tfrac{1}{2}, \tfrac{-1}{2}\rangle + C_{-1,1}|\tfrac{-1}{2}, \tfrac{1}{2}\rangle \tag{45}$$

Because the $|10\rangle$ and $|00\rangle$ states are eigenfunctions of $\hat{S}^2$ with different eigenvalues, they must be orthogonal. Since the functions must also be normalized, we must have $C_{1,-1} = -C_{-1,1}$. This implies that

$$|00\rangle = 2^{-1/2}(|\tfrac{1}{2}, \tfrac{-1}{2}\rangle - |\tfrac{-1}{2}, \tfrac{1}{2}\rangle) \tag{46}$$

The electronic Hamiltonian [Eq. (15)] is symmetric with respect to exchanging the labels of the two electrons. Thus, the wavefunction must be symmetric or antisymmetric with respect to this operation. We see immediately that the three $S = 1$ wavefunctions with $M_S = +1, 0, -1$ are all symmetric, while the $S = 0$ wavefunction is antisymmetric with respect to this interchange. The overall two-electron wavefunction which is a product of a spatial component and a spin-component must be antisymmetric with respect to interchange, since the electrons are fermions. Thus, in cases where the spatial wavefunction is symmetric [as, for example, the ground state of the He atom $1s(1)1s(2)$], the spin wavefunction must be antisymmetric. Hence, the ground state of the He atom must be a $S = 0$ state. This is called a singlet state, because the projection degeneracy of the spin wavefunction, $2M_S + 1$, is equal to 1.

H. Excited states of the He atom

Although the ground state of He must be a singlet, the same is not true of any of the excited states. Consider, for example, the $1s2p$ state, obtained by exciting one of the electrons to the $2p$ state. This transition is analagous to the Lyman α transition in the H atom. There are four possible wavefunctions, which are both antisymmetric with respect to particle exchange. The first is the non-degenerate (singlet) state

$$\left|{}^1 1s2p\right\rangle = 2^{-1/2}[1s(1)2p(2) + 2p(1)1s(2)]|00\rangle$$

The second is for the triplet state, which is triply degenerate, namely

$$\left|{}^3 1s2p\right\rangle = 2^{-1/2}[1s(1)2p(2) - 2p(1)1s(2)]|11\rangle$$

In both cases, the ket on the right-hand-side is the coupled $|SM_S\rangle$ spin function.

The expectation value of the Hamiltonian [Eq. (15)] in these states is

$$\left\langle{}^{1(3)} 1s2p\right| H(1,2) \left|{}^{1(3)} 1s2p\right\rangle = \langle 1s|h|1s\rangle + \langle 2p|h|2p\rangle + [1s^2|2p^2] \pm [1s2p|2p1s] \qquad (47)$$

where the + sign applies to the singlet state and the – sign, to the triplet state. As might be anticipated, the expectation value of the energy is the one-electron energy of each electron, one described by a $1s$ orbital and the other, by a $2p$ orbital. In addition, the two electrons repel one-another, which contributes the $[1s^2|2p^2]$ repulsion term, which is the averaged Coulomb interaction between an electron whose probability distribution is $1s^2$ and an electron whose probability distribution is $2p^2$. Finally, there is the exchange term $[1s2p|2p1s]$. This is a quantum term, which arises because of the requirement that the electrons be indistinguishable.

The exchange term (or "exchange integral") is the self-Coulomb-repulsion of the overlap $1s(1)2p(1)$ charge density. Since this self-repulsion will be a positive quantity, the triplet state will lie lower than the singlet state. This will be true for all the $1snp$ excited states of He. However, since the np orbitals become more and more diffuse as n increases, the overlap charge density will $1s(1)np(1)$ will become smaller and smaller, and hence the $[1snp|np1s]$ exchange integral will become smaller and smaller as n increases. Consequently, the singlet triplet splitting will decrease as the principal quantum number increases.

Problem 12

Consider the $1s2p$ state of a two-electron atom or ion (He, Li$^+$, Be^{++}, B^{+++}). In these systems you have one electron that is close to the nucleus and sees the full nuclear charge while the other electron is far away and sees only a screened nuclear charge of $Z = 1$. Assume that the $1s$ and $2p$ functions are simple hydrogenic orbitals with screening constants ζ_s and ζ_p.

Use this simple picture to estimate for these four two-electron systems

(a) The ζ_s and ζ_p screening constants

(b) The energy (in cm^{-1}) of the $1s2p \rightarrow 1s3p$ transitions. Compare you answers with the experimental numbers from the NIST tables. Note: the experimental triplet $1snp$ states has three spin-orbit components, with slightly different energies. For simplicity, assume the energy is equal to that of the component with J=2.

(c) From Eq. (47) we see that the splitting between the triplet and singlet $1s2p$ states is twice the two-electron exchange integral

$$\Delta E_{31} \equiv E(^1 1s2p) - E(^3 1s2p) = 2[1s2p|2p1s]$$

The value of $[1s2p|2p1s]$ for hydrogenic $1s$ and $2p$ orbitals is

$$[1s_{\zeta_s}2p_{\zeta_p}|2p_{\zeta_p}1s_{\zeta_s}] = \frac{7}{96}\zeta(1+\tau)^3(1-\tau)^5$$

where

$$\tau = (\zeta_s - \zeta_p)/(\zeta_s + \zeta_p)$$

$$\zeta = \frac{1}{2}(\zeta_s + \zeta_p)$$

From your result to part (a), estimate this splitting for He, Li^+, Be^{++}, B^{+++} and compare these estimates with the experimental value of these splittings, which you can get from the NIST tables.

(d) Finally, use the NIST tables to determine the splitting between the triplet and singlet $1snp$ states of He for $n = 2-6$. Plot the results. Plot the experimental triplet-singlet $1snp$ splittings for $n = 2-5$ for He and Li^+.

I. Gaussian orbitals

In application of the Hartree-Fock methodology to many-electron atoms and, especially, molecules, the calculation of two-electron integrals between functions which decrease exponentially in r is very time-consuming. Much faster calculations can be achieved by expansion of the electronic wavefunction as a linear combination of Gaussian functions

$$R(r) = \sum_j C_j \exp(-\alpha_j r^2) \tag{48}$$

rather than the exponential hydrogenic (often called "Slater") orbitals

$$R(r) = \sum_j C_j \exp(-\zeta_j r) \tag{49}$$

Consider, for simplicity, the hydrogen atom. We will expand the $1s$ wavefunction in terms of Gaussian orbitals. The simplest case will be to truncate the series at one term, namely

$$R(r) \approx N_\alpha \exp(-\alpha r^2) \tag{50}$$

where N_α is the normalization constant, chosen to satisfy Eq. (10).

Problem 13

Determine the value of this normalization constant N_α, so that the Gaussian $1s$ function is normalized, namely [Eq. (10)]

$$\langle 1s_\alpha | 1s_\alpha \rangle = \int_0^\infty R(r)^2 r^2 dr = 1 \tag{51}$$

Then, use Matlab to determine an expression for the overlap integral between two Gaussian functions with differing exponential factors

$$S_{\alpha'\alpha} \equiv \langle 1s(\alpha') | 1s(\alpha) \rangle = \int_0^\infty R_\alpha(r) R_{\alpha'}(r) r^2 dr \tag{52}$$

Hint: To check your work, in the limit that the two screening constants are equal

$$\lim_{\alpha'=\alpha} S_{\alpha'\alpha} = 1$$

To determine the energy of the H atom with a single Gaussian approximation to the $1s$ orbital, is is easiest to replace the Gaussian $R(r)$ [Eq. (50)] with $G(r) = rR(r)$ and then evaluate the expectation of the one-electron Hamiltonian of Eq. (13) with $Z = 1$, integrating from 0 to ∞ with an length element of just dr^2 (no factor of r^2). You can use the symbolic algebra feature of Matlab to evaluate the derivatives.

```
syms r

syms alpha

oness=exp(-alpha*r*r)

diff(r^2*diff(oness))/r^2)
```

```
ans =

-((6*alpha*r^2)/exp(alpha*r^2) - (4*alpha^2*r^4)/exp(alpha*r^2))/r^2

simplify(ans)

ans = (2*alpha*(2*alpha*r^2 - 3))/exp(alpha*r^2)
```

Problem 14: Assume that the H atom 1s orbital [Eq. (11)] is described by the single Gaussian of Eq. (50). In problem 13 have already determined the normalization constant in terms of α. Then, determine an expression for the variational energy of the H atom as a function of α. At what value of α is the energy lowest? What is the value of this best variational energy? Remember that the variational principle guarantees that this value should always be greater than the true electronic energy of the 1s electron in the H atom, namely –0.5 Hartree.

Let's compare the Gaussian approximation to the 1s orbital with $g(r)$ for the true 1s orbital of H, which is

$$g_{1s}(r) = 2r\exp(-r) \tag{53}$$

This expression is normalized, so that $\int_0^\infty g_{1s}(r)^2 dr = 1$.

Problem 15:

(a) Plot your best single-Gaussian function (Prof. 14) compared to the true 1s orbital. Make sure to label your axes!

(b) A variational calculation was done with a three-Gaussian approximation to the 1s orbital

$$g_{1s} \approx \sum_{i=1}^{N} C_i N_i r\exp(-\alpha_i r^2) \tag{54}$$

with

$$\alpha = [4.502, 0.681, \text{ and } 0.151]$$

The variational energy is –0.49698 and expansion coefficients were found to be:

$$C = \{0.070426622, 0.408558457, 0.647278802\}$$

> Plot this 3-function Gaussian approximation to the 1s orbital and compare it to the exact 1s function.

J. Coupling of two angular momenta

For reference, the angular momentum raising and lowering operators are defined by

$$\mathrm{J}_\pm|jm\rangle = \left[j(j+1)-m(m\mp1)\right]^{1/2}|j,m\pm1\rangle\,. \tag{55}$$

Now, consider two angular momenta $\vec{j}_1$ and $\vec{j}_2$. The so-called "uncoupled states" are the products of the angular momentum states associated with each operator, namely

$$|j_1m_1j_2m_2\rangle \equiv |j_1m_1\rangle\,|j_2m_2\rangle$$

There are $(2j_1+1)(2j_2+1)$ of these product states, each of which is an eigenfunction of the operators j_{1z}, j_1^2, j_{2z}, j_2^2.

Now consider the total angular momentum $\vec{J}=\vec{j}_1+\vec{j}_2$ and its projection $J_z = j_{1z}+j_{2z}$. Since any component of $\vec{j}_1$, as well as its square, commutes with any component of $\vec{j}_2$, because they operate in different spaces, you can show that j_1^2 and j_2^2 commute with both J_z and J^2. However,

$$J^2 = j_1^2+j_2^2+2\vec{j}_1\cdot\vec{j}_2 = j_2^2+j_2^2+2\left(j_{1x}j_{2x}+j_{1y}j_{2y}+j_{1z}j_{2z}\right)$$

Since j_{1z} does not commute with either j_{1x} or with j_{1y}, it is clear that neither j_{1z} nor j_{2z} commute with J^2. We can thus replace the four commuting operators j_{1z}, j_1^2, j_{2z}, j_2^2 with another set of four commuting operators J^2, J_z, j_{2z}, j_2^2. The eigenfunctions of this latter set of operators are called "coupled states" and are designated $|j_1j_2JM\rangle$. The two sets of eigenfunctions must be related by an orthogonal transformation, namely

$$|j_1j_2JM\rangle = \sum_{m_1\,m_2} C_{j_1m_1j_2m_2,JM}\,|j_1m_1j_2m_2\rangle \equiv \sum_{m_1\,m_2}\left(j_1m_1j_2m_2\,|JM\right)|j_1m_1j_2m_2\rangle \tag{56}$$

The coefficients which appear on the right-hand side are called Clebsch-Gordan (CG) coefficients, and are designated $(j_1 m_1 j_2 m_2 \,| JM)$. Because $\vec{J} = \vec{j}_1 + \vec{j}_2$, it follows that $J_z = j_{1z} + j_{2z}$. It then follows that $M = m_1 + m_2$, in other words, the projection of the total spin equals the sum of the individual projection quantum numbers. This relation can be ensured by requiring that the CG coefficients vanish unless $m_1 + m_2 = M$. Further, we assume that both the coupled and uncoupled states are normalized and orthogonal, in other words

$$\langle j_1 j_2 J' M' \,| j_1 j_2 J M \rangle = \delta_{J,J'} \delta_{M,M'} \tag{57}$$

and

$$\langle j_1 m_1' j_2 m_2' \,| j_1 m_2 j_2 m_2 \rangle = \delta_{m_1,m_1'} \delta_{m_2,m_2'} \tag{58}$$

These two equations, along with Eq. (56), can be used to derive the two orthogonality relations for the CG coefficients:

$$\sum_{m_1,m_2} (j_1 m_1 j_2 m_2 \,| JM)\, (j_1 m_1 j_2 m_2 \,| J' M') = \delta_{J,J'} \delta_{M,M'}$$

and

$$\sum_{m_1,m_2} (j_1 m_1 j_2 m_2 \,| JM)\, (j_1 m_1 j_2 m_2 \,| J' M') = \delta_{J,J'} \delta_{M,M'}$$

and

$$\sum_{J,M} (j_1 m_1 j_2 m_2 \,| JM)\, (j_1 m_1' j_2 m_2' \,| JM) = \delta_{m_1,m_1'} \delta_{m_2,m_2'}$$

Because the transformation of Eq. (56) is an orthogonal transformation, its inverse is just the transpose of the matrix of CG coefficients, assuming that they are real

Consider, for illustration, the case where $j_1 = 2$ and $j_2 = 1$. The following figures shows all the possible values of m_1 and m_2. Each filled circle indicates one of the $|j_1 m_1 j_2 m_2\rangle$ uncoupled states. There are $(2j_1 + 1)(2j_2 + 1) = 15$ of these. The largest value of $M = m_1 + m_2$ is 3. The next value is $M = 2$ and so forth. The diagonal red lines connect all the possible states for each indicated value of M. There is one state for $M = 3$, two for $M = 2$, three for $M = 1$ and so forth.

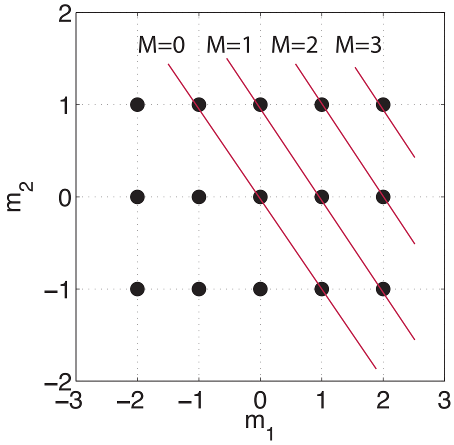

FIG. 6. Illustration of all uncoupled states for $j_1 = 2$ and $j_2 = 1$.

K. Determination of Clebsch-Gordan coefficients

To determine the Clebsch-Gordan coefficients we start with the largest value of J and M. As we can see in Fig. 6, this is $J = j_1 + j_2$ ($J = 3$ in the example shown) and $M = j_1 + j_2$. Since there is only one uncoupled state which satisfies these criteria – the so-called "stretched" state – Eq. (56) reduces to

$$|j_1j_2, J = j_1 + j_2, M = j_1 + j_2\rangle_c = (j_1j_1j_2j_2\,|j_1 + j_2, j_1 + j_2)\,|j_1j_1j_2j_2\rangle_u \tag{59}$$

Here the subscripts c and u will designate the coupled and uncoupled states. Since both the uncoupled and coupled states are assumed normalized, the coefficient has to equal one (at least in magnitude). Thus we can say, choosing the phase factor to be +1,

$$(j_1j_1j_2j_2\,|j_1 + j_2, j_1 + j_2) = 1$$

Now, let us operate on both the left and the right hand sides of Eq. (59) with the lowering operator $J_- = j_{1-} + j_{2-}$. This gives for the operation of J_- on the coupled state (the left-hand side)

$$\begin{aligned}&[J(J+1) - M(M-1)]^{1/2}\,|j_1j_2, J = j_1 + j_2, M = j_1 + j_2 - 1\rangle_c\\&= [(j_1 + j_2)(j_1 + j_2 + 1) - (j_1 + j_2)(j_1 + j_2 - 1)]^{1/2}\,|j_1j_2, J = j_1 + j_2, M = j_1 + j_2 - 1\rangle_c\\&= [2(j_1 + j_2)]^{1/2}\,|j_1j_2, j_1 + j_2, j_1 + j_2 - 1\rangle_c\end{aligned} \tag{60}$$

and, for the action of J_- on the uncoupled state (the right-hand side)

$$\begin{aligned}
&J_- \left|j_1 j_1 j_2 j_2\right\rangle_u = (j_{1-} + j_{2-}) \left|j_1 j_1 j_2 j_2\right\rangle_u \\
&= \left[j_1(j_1+1) + j_1(j_1-1)\right]^{1/2} \left|j_1, j_1-1, j_2 j_2\right\rangle_u + \left[j_2(j_2+1) + j_2(j_2-1)\right]^{1/2} \left|j_1 j_1 j_2, j_2-1\right\rangle_u \\
&= \sqrt{2j_1} \left|j_1, j_1-1, j_2 j_2\right\rangle_u + \sqrt{2j_2} \left|j_1 j_1 j_2, j_2-1\right\rangle_u \qquad (61)
\end{aligned}$$

Equating the two previous equations gives

$$[2(j_1+j_2)]^{1/2} \left|j_1 j_2, j_1+j_2, j_1+j_2-1\right\rangle_c = \sqrt{2j_1} \left|j_1, j_1-1, j_2 j_2\right\rangle_u + \sqrt{2j_2} \left|j_1 j_1 j_2, j_2-1\right\rangle_u$$

or

$$\left|j_1 j_2, j_1+j_2, j_1+j_2-1\right\rangle_c = \left[\frac{j_1}{j_1+j_2}\right]^{1/2} \left|j_1, j_1-1, j_2 j_2\right\rangle_u + \left[\frac{j_2}{j_1+j_2}\right]^{1/2} \left|j_1 j_1 j_2, j_2-1\right\rangle_u \qquad (62)$$

The two terms on the right-hand side must be the CG coefficients as defined in Eq. (56). Thus, we see that

$$(j_1, j_1-1, j_2, j_2 \left| j_1+j_2, j_1+j_2-1\right.) = \left[\frac{j_1}{j_1+j_2}\right]^{1/2}$$

and

$$(j_1, j_1, j_2, j_2-1 \left| j_1+j_2, j_1+j_2-1\right.) = \left[\frac{j_2}{j_1+j_2}\right]^{1/2}$$

Explicitly, in the case where $j_1 = 2$ and $j_2 = 1$ (as in Fig. 6), we have

$$\begin{aligned}
\left|2132\right\rangle_c &= (2111|32)|2111\rangle_u + (2210|32)|2210\rangle_u \\
&= (2/3)^{1/2}|2111\rangle_u + (1/3)^{1/2}|2210\rangle_u \qquad (63)
\end{aligned}$$

By continuing the application of $J_- = j_{1-} + j_{2-}$, we can generate all the GC coefficients for $J = j_1 + j_2$ for all allowed values of M ($M = j_1+j_2-2, j_1+j_2-3, ..., -j_1-j_2+1, -j_1-j_2$).

Now, we need the Clebsch-Gordan coefficients for the next lower value of J, namely $J = j_1 + j_2 - 1$. For this value of J, the highest value of M is $j_1 + j_2 - 1$. In this case, Eq. (56) reads

$$\begin{aligned}|j_1j_2, j_1+j_2-1, j_1+j_2-1\rangle_c &= (j_1j_1-1j_2j_2\,|j_1+j_2-1, j_1+j_2-1)\,|j_1, j_1-1, j_2j_2\rangle_u \\ &\quad + (j_1j_1j_2j_2-1\,|j_1+j_2-1, j_1+j_2-1)\,|j_1j_1j_2, j_2-1\rangle_u \end{aligned} \tag{64}$$

Now, the left hand sides of Eqs. (62) and (64) must be orthogonal, because $J = j_1 + j_2$ for the first and $J = j_1 + j_2 - 1$. Consequently, the right hand sides must also be orthogonal. Since the functions must also be normalized, it is clear that

$$(j_1j_1-1j_2j_2\,|j_1+j_2-1, j_1+j_2-1) = \pm\left[\frac{j_2}{j_1+j_2}\right]^{1/2} \tag{65}$$

and

$$(j_1j_1j_2j_2-1\,|j_1+j_2-1, j_1+j_2-1) = \mp\left[\frac{j_1}{j_1+j_2}\right]^{1/2} \tag{66}$$

To make things more concrete, in the case where $j_1 = 2$ and $j_2 = 1$ we have

$$\begin{aligned}|2122\rangle_c &= (2111|22)|2111\rangle_u + (2210|22)|2210\rangle_u \\ &= \pm(1/3)^{1/2}|2111\rangle_u \mp (2/3)^{1/2}|2210\rangle_u\end{aligned} \tag{67}$$

The sign is established by the so-called Condon and Shortley phase convention that *all matrix elements of j_{1z}, which are non-diagonal in J, are real and non-negative.* [2] Consider, then, the matrix element

$$\begin{aligned}\langle 2132|\,l_{1z}\,|2122\rangle_u &= \pm\frac{2^{1/2}}{3}\langle 2111|l_{1z}|2111\rangle_u \mp \frac{2^{1/2}}{3}\langle 2210|l_{1z}|2210\rangle_u \\ &\quad \mp\frac{2}{3}\langle 2111|l_{1z}|2210\rangle_u \pm \frac{1}{3}\langle 2210|l_{1z}|2111\rangle_u\end{aligned} \tag{68}$$

Now, we know that (suppressing the $\hbar$) $l_{1z}|2111\rangle_u = |2111\rangle_u$ and $l_{1z}|2210\rangle_u = 2|2110\rangle_u$. Thus we find

$$\langle 2111|l_{1z}|2111\rangle_u = +1\,,$$

$$\langle 2210|l_{1z}|2210\rangle_u = +2\,,$$

$$\langle 2210|l_{1z}|2111\rangle_u = \langle 2210|2111\rangle_u = 0\,,$$

and

$$\langle 2111|l_{1z}|2210\rangle_u = \langle 2111|2211\rangle_u = 0\,,$$

Thus, we find that

$$\langle 2132|\, l_{1z}\, |2122\rangle_u = \pm\frac{2^{1/2}}{3} \mp 2\frac{2^{1/2}}{3} = \mp\frac{2^{1/2}}{3} \tag{69}$$

Consequently, for the Condon-Shortley phase convention to be satisfied we have to chose the lower sign in Eqs. (65) and (66), so that

$$(2111|22) = -\left(\frac{1}{3}\right)^{1/2}$$

and

$$(2210|22) = +\left(\frac{2}{3}\right)^{1/2}$$

Problem 16 You know that $|2133\rangle_c$ (the stretched state) $= |2211\rangle_u$. The expression for $|2132\rangle_c$ is given by Eq. (63). By repeated application of the lowering operator, generate the CG coefficients for $j_1 = 2$, $j_2 = 1$, $J = 3, M$ for $M = 1$ and $M = 0$.

Problem 17 For $j_1 = 2$ and $j_2 = 1$ the lowest allowed value of J is 1. In problem 16 you have obtained the expression for the $|2131\rangle_c$ state in terms of uncoupled states. The comparable expression for the $|2121\rangle_c$ state is

$$|2121\rangle_c = -2^{-1/2}|2011\rangle_u + 6^{-1/2}|2110\rangle_u + 3^{-1/2}|221-1\rangle_u$$

For $J = 1$, the comparable expression would be

$$|2121\rangle_c = a|2011\rangle_u + b|2110\rangle_u + c|221-1\rangle_u$$

By requiring the state $|2111\rangle_c$ to be (a) normalized and (b) orthogonal to the $J = 3$ and $J = 2$ states with $M = 1$, you can determine the values of the coefficients a, b, and c, to within an arbitrary sign. To fix the sign, you can impose the Condon-Shortley phase convention, requiring that

$$\langle 2121|l_{1z}|2111\rangle_c \geq 0$$

The coefficients a, b, and c, are, in fact, the CG coefficients $(2011|11)$, $(2110|11)$, and $(221-1|11)$. *Hint*: the value of $(2011|11)$ is $(1/10)^{1/2}$.

L. Multi-electron atoms

1. Permutation symmetry

For an N-electron atomic or molecular system with $N \geq 2$, the Hamiltonian is the extension of Eq. (15), namely

$$H(r_1, \ldots, r_N) = \sum_{i=1}^{N} h(\vec{r}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \frac{1}{r_{ij}}$$

where $r_{ij} = |\vec{r}_i - \vec{r}_j|$. The Hamiltonian is a sum of one-electron terms (kinetic energy plus the attraction of the electron to the nucleus) plus a sum of pairwise repulsions between the electrons. The Hamiltonian is unchanged by an exchange of the labels of any two electrons. This is called a permutation. The permutation operator $\hat{P}_{ij}$ exchanges the labels of electrons i and j. Since the Hamiltonian commutes with the permutation operator, the wave function can be simultaneously an eigenfunction of $\hat{H}$ and $\hat{P}$. Since electrons are fermions, the eigenrelation must be

$$\hat{P}_{ij}\Psi(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_j, \ldots, r_N) = -\Psi(\vec{r}_1, \ldots, \vec{r}_j, \ldots, \vec{r}_i, \ldots, r_N) \tag{70}$$

For an N-electron system, as in the case of the He atom, a simple approximation to the electronic wavefunction is as a product of one-electron functions $\phi_1(\vec{r}_1)\ldots\phi_N(\vec{r}_N)$. In fact, it is this simple product-of-one-electron-functions approximation that enables all of chemistry to visualize and understand the electronic structure of atoms and molecules. In addition to the spatial coordinates of each electron $\vec{r}$, we need to specify its spin. We designate by the name “spin-orbital” the product of the spatial function $\phi_i(\vec{r})$ and a spin eigenfunction. Consider, then, a set of N one-electron spin-orbitals $\{\varphi_1, \varphi_2, \ldots\varphi_{N-1}, \varphi_N\}$, where

$$\varphi_i \equiv \phi_i(\vec{r})\,|sm_s\rangle\,.$$

Here $|sm_s\rangle$ designates the total spin s and its projection m_s. For an electron $s = 1/2$ and $m_s = \pm 1/2$. You will often see the compact notation

$$\varphi_i \equiv \phi_i(\vec{r})$$

or

$$\varphi_i \equiv \bar{\phi}_i(\vec{r})$$

Here the superscript bar indicates $m_s = -1/2$ (down spin) and the absence of a bar indicates $m_s = +1/2$ (up spin). We assume that these functions are orthogonal and normalized, so that $\int \varphi_i^* \varphi_j dV ds = \delta_{ij}$. Note that we are integrating over both the spatial and spin degrees of freedom of the electron. The simple product-of-one-electron-functions approximation of the N-electron wave function is, mathematically.

$$\Psi(\vec{r}_1, \ldots, \vec{r}_i, \ldots, \vec{r}_j, \ldots, r_N) = \phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\ldots\phi_N(\vec{r}_N) \tag{71}$$

But this function doesn't satisfy fermion permutation requirement of Eq. (70). For example, suppose we permute labels 1 and 2. Then

$$\hat{P}_{12}\phi_1(\vec{r}_1)\phi_2(\vec{r}_2)\ldots\phi_N(\vec{r}_N) = \phi_2(\vec{r}_1)\phi_1(\vec{r}_2)\ldots\phi_N(\vec{r}_N)$$

This does not satisfy Eq. (70). On the left-hand-side, electron 1 is associated with spin-orbital 1 and electron 2 with spin-orbital 2. On the right-hand-side, electron 1 is associated with spin-orbital 2 while electron 2 is associated with spin-orbital 1. This is not the same thing, even if we introduce a minus sign.

In the case of the He atom (Sec. I G), to satisfy the requirement of permutation antisymmetry we expressed the electronic wave function as a product of a symmetric spatial function multiplied by an antisymmetric spin function, or vice versa. This separation is unfortunately not possible for systems with more than 2 electrons.

2. Slater determinants – Li atom

Luckily, there is a straight forward modification of the simple product [Eq. (71)] which does satisfy the required permutation antisymmetry. This is done by writing the wave function as a "Slater determinant". We'll use the Li atom as an illustration. The electron configuration is $1s^2 2s$, or, in terms of spin-orbitals $1s1\bar{s}2s$. The Slater determinantal notation is

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) \equiv \Psi(1,2,3) = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1) & 1\bar{s}(1) & 2s(1) \\ 1s(2) & 1\bar{s}(2) & 2s(2) \\ 1s(3) & 1\bar{s}(3) & 2s(3) \end{vmatrix} \tag{72}$$

where $|\,|$ denotes a determinant. We've also simplified the notation a bit by replacing the electronic coordinates $\vec{r}_1 \equiv \{r_1, \theta_1, \phi_1\}$ by the single index "1". Expanding the determinant will give 6 terms, involving all the possible permutation of the three electrons between the three spin-orbitals. We have

$$\begin{aligned} \Psi(1,2,3) = 6^{-1/2}[&1s(1)\bar{1}s(2)2s(3) + 1s(3)\bar{1}s(1)2s(2) + 1s(2)\bar{1}s(3)2s(1) \\ &-1s(3)\bar{1}s(2)2s(1) - 1s(2)\bar{1}s(1)2s(3) - 1s(1)\bar{1}s(3)2s(2)] \end{aligned} \tag{73}$$

Note that all terms involving a single permutation appear with a minus sign and all terms involving a double permutation appear with a positive sign.

The permutation symmetry is guaranteed by the choice of a determinant to represent the wave function: Interchanging the labels of any two electrons involves interchanging two rows of the determinant in Eq. (72). For a determinant, interchanging any two rows changes the sign of the determinant.

For the Li atom the electronic Hamiltonian is

$$\hat{H}(1,2,3) = h(1) + h(2) + h(3) + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}}$$

The variational energy is $\langle \Psi(1,2,3) \left| \hat{H}(1,2,3) \right| \Psi(1,2,3) \rangle$. From Eq. (73) we see that this will involve $6 \times 6 = 36$ terms. The Hamiltonian is a sum of one-electron and two-electron terms. We'll assume that the spin-orbitals are orthogonal (and normalized). If that's the case, then the one electron terms will contribute only diagonally, in other words when the occupancy of the spin-orbitals is identical on the left and right hand sides. That's because any permutation involves a switch of two indices. So for the one electron terms, the orthogonality of the 2nd index will cause the term to vanish. For example, consider the term

$$\begin{aligned}\langle 1s(1)\bar{1}s(2)2s(3)\,|\,h(1)\,|\,\hat{P}_{12}[1s(1)\bar{1}s(2)2s(3)]\rangle &= \langle 1s(1)\bar{1}s(2)2s(3)\,|\,h(1)\,|\,1s(2)\bar{1}s(1)2s(3)\rangle \\ &= \int 1s(1)^* h(1)\bar{1}s(1)dV_1 ds_1 \int \bar{1}s(2)^* 1s(2)dV_2 ds_2 \int 2s(3)^* 2s(3)dV_3 ds_3 \qquad (74)\end{aligned}$$

The 2^{nd} integral will vanish since the spin-projection quantum number differs in the bra and ket components. There will be 6 diagonal terms, which will each give the same result. But the normalization constant is $6^{-1/2}$. So the square of this normalization constant will exactly cancel the 6-fold redundancy.

Similarly, the two-electron terms will contribute to the 6 diagonal terms and to the terms in which the same electron pair is permuted on the left- and right- hand sides. The net result is that the expectation value of the Hamiltonian is

$$\left\langle \Psi(1,2,3)\ \middle|\ \hat{H}(1,2,3)\middle|\ \Psi(1,2,3)\right\rangle = 2h_{1s} + h_{2s} + [1s1s|1s1s] + 2\,[1s1s|2s2s] - [1s2s|2s1s] \qquad (75)$$

where

$$h_{1s} = \int 1s(1)h(1)1s(1)d\tau_1 = \int 1s(2)h(2)1s(2)d\tau_2 = \int 1s(3)h(3)1s(3)d\tau_3 \qquad (76)$$

and, similarly, for h_{2s}. We have introduced here a general, compact notation for the two-electron integrals

$$[\varphi\varphi\,|\chi\chi] = \iint \varphi(1)^*\varphi(1)\frac{1}{r_{12}}\chi(2)^*\chi\,(2)\,d\tau_1 d\tau_2 \qquad (77)$$

and

$$[\varphi\chi\,|\chi\varphi] = \iint \varphi(1)^*\chi(1)\frac{1}{r_{12}}\chi(2)^*\varphi\,(2)\,d\tau_1 d\tau_2 \qquad (78)$$

The expression for the matrix element of the Hamiltonian in Eq. (75) has a simple physical interpretation. In the Li atom there are two electrons in the $1s$ orbital and one electron in the $2s$ orbital. Each electron has a one-electron energy (kinetic energy plus attraction to the nucleus). Thus, the one-electron contribution is $2h_{1s} + h_{2s}$ (because there are two $1s$ electrons, there is a factor of 2 in front of the h_{1s} term.

In addition, every electron is repelled by every other electron. There is one $1s - 1s$ repulsion and two $1s - 2s$ repulsions. Thus, Eq. (75) contains a total Coulomb repulsion energy of $[1s1s|1s1s] + 2[1s1s|2s2s]$. Finally, there is a purely quantum correction to the energy, which is a consequence of the requirement that the wave function be antisymmetric. This correction is: for every pair of electrons that have the same spin, there is a negative so-called "exchange" contribution to the energy, namely $[\varphi\chi|\chi\varphi]$, or, specifically in the case of Li, $[1s2s|2s1s]$.

Problem 18 A simpler notation for the determinantal wave function of Eq. (72) is

$$\psi(1,2,3) = |1s\bar{1}s2s| \tag{79}$$

Here the vertical bars denote a Slater determinant with normalization factor of $(N!^{-1/2})$, and we list the spin-orbitals which are occupied.

(a) Write down an expression similar to Eq. (79) for the electronic wave function of the B atom.

(b) Then give an expression of the electronic energy of the B atom similar to Eq. (75).

3. Slater Determinants – General

In general, for N electrons we'll have an $N \times N$ determinant,

$$\Psi(1,2,\ldots,N) = (N!)^{-1/2} \begin{vmatrix} \phi_1(1) & \phi_2(1) & \cdots & \phi_N(1) \\ \phi_1(2) & \phi_2(2) & \cdots & \phi_N(2) \\ \vdots & \vdots & \vdots & \vdots \\ \phi_1(N) & \phi_2(N) & \cdots & \phi_N(N) \end{vmatrix} \tag{80}$$

Or, following Eq. (79), we can simplify this notation to

$$\Psi(1,2,\ldots,N) = |\phi_1\phi_2\cdots\phi_N| \tag{81}$$

In the Appendix on Slater Determinants we discuss how the energy is

$$\begin{aligned}\langle\Psi(1,\ldots,N)|\hat{H}(1,\ldots,N)|\Psi(1,\ldots,N)\rangle &= \sum_{i=1}^{N}\langle\phi_i|\hat{h}|\phi_i\rangle + \sum_{i=1}^{N-1}\sum_{j=2}^{N}\Big([\phi_i\phi_i|\phi_j\phi_j] - \delta_{m_{s_i},m_{s_j}}[\phi_i\phi_j|\phi_j\phi_i]\Big)\\ &= \sum_{i=1}^{N} h_i + \sum_{i=1}^{N-1}\sum_{j=2}^{N}\Big([\phi_i^2|\phi_j^2] - \delta_{m_{s_i},m_{s_j}}[\phi_i\phi_j|\phi_j\phi_i]\Big) \qquad (82)\end{aligned}$$

Again,

1. Every electron has a one electron energy, so there is an h_i term for each spin orbital.
2. All pairs of electrons repel one another, so that there are $N(N-1)/2$ $[\phi_i^2|\phi_j^2]$ terms.
3. For every pair of electrons *that have the same spin*, there is a negative exchange term $-[\phi_i\phi_j|\phi_j\phi_i]$.

4. Slater determinants – C atom

Now, consider the carbon atom ($1s^2 2s^2 2p^2$). Here two of the six $2p$ orbitals are filled. As we will discuss in more detail, there is more than one $1s^2 2s^2 2p^2$ electronic states, which differ in energy. At a basic level, there are three $2p$ orbitals and two ($m_s = \pm 1/2$) possible spin states for each electron. Thus there are $2\times 3 = 6$ possible spin orbitals. By the Pauli exclusion principle at most one electron can be assigned to each spin-orbital. The first electron can occupy one of 6 spin orbitals and the second electron, any of the remaining 5. Thus there are 30 possibilities. Because the two electrons are indistinguishable, we can eliminate 1/2 of these by symmetry, which leaves 15. Not all correspond to states of different energies. Many of the 15 possible electron assignments are degenerate. The easiest way to sort this out is by application of the tableau method.

From this supplemental chapter, we deduce that the 15 different electron assignments correspond to nine ^3P states with $L = 1, S = 1$, five ^1D states with $L = 1, S = 0$ and one ^1S state with $L = 0, S = 0$. We can use a simplified Slater determinantal notation for the wave functions for each of these states, which we designate $^{2S+1}L_{M_L,M_S}$. For example, the ^3P state with $M_L = 1$ and $M_S = 1$ corresponds to $1s^2 2s^2 2p_1 2p_0$, where the spins of both $2p$

electrons are $m_s = 1/2$. The Slater determinant for this state is

$$\left|{}^3P_{11}\right\rangle = |1s\bar{1}s2s\bar{2}s2p_02p_1| \tag{83}$$

For simplicity, we can suppress the $1s$ and $2s$ spin-orbitals and write this as

$$\left|{}^3P_{11}\right\rangle = |p_1p_0| \tag{84}$$

The wavefunctions for the other ${}^{(2S+1)}L_{M_L,M_S}$ states can be obtained by application of the S_- and L_- lowering operators. Each of these is the sum of the raising or lowering operators for each of the electrons. In general

$$\hat{L}_- = \sum_{i=1}^{N} \hat{l}_{i-}$$

and similarly for $\hat{L}_+$, $\hat{S}_-$ and $\hat{S}_+$. Thus, for example, for the $2p^2$ C atom

$$L_- \left|{}^3P_{11}\right\rangle = (l_{1-} + l_{2-})\,|p_1p_0| \tag{85}$$

Now, the general effect of a lowering operator is [see Eq. (550]

$$l_-|lm_l\rangle = [l(l+1) - m_l(m_l-1)]^{1/2}$$

For example $l_{1-}\,|p_1p_0| = 2^{1/2}\,|p_0p_0|$. This vanishes, because the 5^{th} and 6^{th} columns of the Slater determinant are equal and any determinant vanishes if two columns are the same. However, $l_{2-}\,|p_1p_0| = 2^{1/2}\,|p_1p_1|$, which does not vanish. Similarly, $L_-\,|{}^3P_{11}\rangle = 2^{1/2}\,|{}^3P_{01}\rangle$. Thus, we find that

$$\left|{}^3P_{01}\right\rangle = |p_1p_{-1}| \tag{86}$$

Note that we don't need to operate on the $1s$ or $2s$ spin-orbitals with the lowering operators because l_- operating on an s function ($l = 0$) gives zero and s_- gives either zero or leads to two identical columns.

Problem 19 : (a) Determine the determinantal wavefunctions for the other C ^3P states. Write these wavefunctions in the simplified $|p_ip_j|$ notation of Eqs. (86) and (87). The other ^3P wavefunctions can be generated, as above, by application of L_- and S_-.
(b) Do the same for the ^1D wavefunctions. You can generate these starting with

$$\left|{}^1D_{20}\right\rangle = |p_1\bar{p}_1| \tag{87}$$

and then using L_-. Note, that the wavefunctions for M_L and/or $M_S < 0$ can be generated almost by inspection from those with M_L and/or $M_S > 0$.

Here is an example to help you solve this problem:

$$\begin{aligned}\left|{}^3P_{00}\right\rangle &= S_- \left|{}^3P_{01}\right\rangle = (s_{1-} + s_{2-})|p_1p_{-1}| \\ &= N\left(|\bar{p}_1p_{-1}| + |p_1\bar{p}_{-1}|\right) = N\left(-|p_{-1}\bar{p}_1| + |p_1\bar{p}_{-1}|\right) \\ &= 2^{-1/2}\left(-|p_{-1}\bar{p}_1| + |p_1\bar{p}_{-1}|\right) \end{aligned} \tag{88}$$

Here, the normalization constant can be obtained from the applications of S_- on the left, which gives a factor of $[S(S+1)-M_S(M_S-1)]^{1/2} = \sqrt{2}$ on the left, and the applications of $s_{1-}+s_{2-}$ on the right, each of which give a factor of $[s(s+1)-m_s(m_s-1)]^{1/2} = 1$ on the right. Alternatively, and more simply, N is fixed so the the sum of Slater determinants is normalized, namely [for Eq. (88)], $N = 2^{-1/2}$.

Similarly, we obtain

$$\left|{}^1D_{10}\right\rangle = L_- \left|{}^1D_{20}\right\rangle = (l_{1-} + l_{2-})|p_1\bar{p}_1| = 2^{-1/2}\left(|p_0\bar{p}_1| + |p_1\bar{p}_0|\right)$$

and

$$\begin{aligned}\left|{}^1D_{00}\right\rangle &= L_- \left|{}^1D_{10}\right\rangle = N\left(|p_{-1}\bar{p}_1| + |p_0\bar{p}_0| + |p_0\bar{p}_0| + |p_1\bar{p}_{-1}|\right) \\ &= 6^{-1/2}\left(|p_{-1}\bar{p}_1| + |p_1\bar{p}_{-1}| + 2|p_0\bar{p}_0|\right)\end{aligned} \tag{89}$$

Here, the normalization constant has to be $1/\sqrt{6}$.

The single $^1S_{00}$ wavefunction (only $M_L = M_S = 0$ is allowed) must also be a linear combination of the three Slater determinants ($|p_1\bar{p}_{-1}|$, $|p_{-1}\bar{p}_1|$, and $|p_0\bar{p}_0|$) which have

$M_S = 0$ and $M_L = 0$. We have

$$\left|{}^1S_{00}\right\rangle = a|p_1\bar{p}_{-1}| + b|p_{-1}\bar{p}_1| + c|p_0\bar{p}_0| \tag{90}$$

The coefficients must be chosen so that this function is orthogonal to the Slater determinant expansion of the wave functions for the $|{}^1D_{00}\rangle$ and $|{}^3P_{00}\rangle$ states [Eqs. (89) and (88).

(c) What are the values of a, b, and c?

5. *Conversion from definite-M to Cartesian orbitals*

It is often convenient to express these wavefunctions in terms of the real (Cartesian) p_x and p_y orbitals rather than the complex p_1 and p_{-1} orbitals. Remember that $p_z = p_0$. Since (note the minus sign for p_x, this arises because of the phase conventions of the spherical harmonics)

$$p_1 = -2^{-1/2}\left(p_x + ip_y\right) \text{ and } p_{-1} = 2^{-1/2}\left(p_x - ip_y\right) \tag{91}$$

we can transform all the wavefunctions into representations in terms of the Cartesian spin-orbitals. For example

$$\left|{}^1D_{20}\right\rangle = |p_1\bar{p}_1| = 2^{-1}\left[|p_x\bar{p}_x| - |p_y\bar{p}_y| + i\,|p_x\bar{p}_y| + i\,|p_y\bar{p}_x|\right] \tag{92}$$

Similarly, we find for the ${}^1D$ state with $M_L = -2$

$$\left|{}^1D_{-2,0}\right\rangle = |p_{-1}\bar{p}_{-1}| = 2^{-1}\left[|p_x\bar{p}_x| - |p_y\bar{p}_y| - i\,|p_x\bar{p}_y| - i\,|p_y\bar{p}_x|\right] \tag{93}$$

If you take the normalized plus and minus linear combination of these two states, you obtain

$$\left|{}^1D_{x^2-y^2}\right\rangle = 2^{-1/2}\left(\left|{}^1D_{20}\right\rangle + \left|{}^1D_{-2,0}\right\rangle\right) = 2^{-1/2}\left[|p_x\bar{p}_x| - |p_y\bar{p}_y|\right] = 2^{-1/2}[\,|x\bar{x}| - |y\bar{y}|\,] \tag{94}$$

and

$$\left|{}^1D_{xy}\right\rangle = -i2^{-1/2}\left(\left|{}^1D_{20}\right\rangle - \left|{}^1D_{-2,0}\right\rangle\right) = 2^{-1/2}\left[|p_x\bar{p}_y| + |p_y\bar{p}_x|\right] = 2^{-1/2}[\,|x\bar{y}| + |y\bar{x}|\,] \tag{95}$$

You can show that the energy of the ${}^1D_{x^2-y^2}$ state is

$$\begin{aligned} E({}^1D_{x^2-y^2}) = {} & 2\varepsilon_{1s} + 2\varepsilon_{2s} + 2\varepsilon_{2p} + [1s^2|1s^2] + [2s^2|2s^2] + 4[1s^2|2s^2] + 4[1s^2|2p_x^2] + 4[2s^2|2p_x^2] \\ & -2[1s2s|2s1s] - 2[1s2p_x|2p_x1s] - 2[2s2p_x|2p_x2s] \\ & +[2p_x^2|2p_x^2] - [2p_x2p_y|2p_y2p_x] \end{aligned} \tag{96}$$

Note that $[a^2|b^2] = [b^2|a^2]$. Also, because the x, y, and z directions are equivalent

$$[s^2|2p_x^2] = [s^2|2p_y^2] \tag{97}$$

and

$$[s2p_x|2p_xs] = [s2p_y|2p_ys]$$

Finally,

$$[1s2p_x|2p_y1s] = [2s2p_x|2p_y2s] = 0$$

This vanishing reflects the fact that the product of an s and a Cartesian $2p_x$ orbital is antisymmetric with respect for reflection in the yz plane, which the product of an s and a $2p_y$ orbital is symmetric with respect to the same reflection.

The contribution of the $1s$ and $2s$ electrons to the 15 states of the C atom are all identical (as you might expect, because of the spherical symmetry of the s orbitals. Thus, you could simplify Eq. (98) to read

$$E({}^1D_{x^2-y^2}) = E_C + [2p_x^2|2p_x^2] - [2p_x2p_y|2p_y2p_x] = E_C + [x^2|x^2] - [xy|yx] \tag{98}$$

where

$$\begin{aligned} E_C = {} & 2\varepsilon_{1s} + 2\varepsilon_{2s} + 2\varepsilon_{2p} + [1s^2|1s^2] + [2s^2|2s^2] + 4[1s^2|2s^2] + 2[1s^2|2p_x^2] + 2[2s^2|2p_x^2] \\ & -2[1s2s|2s1s] - 2[1s2p_x|2p_x1s] - 2[2s2p_x|2p_x2s] \end{aligned} \tag{99}$$

We see from Eq. (98) that the energy of any of the states of the C atom is equal to a common value (E_C) plus the expectation value of r_{12}^{-1} (the electron repulsion) between the two $2p$ electrons.

Similarly, from Eq. (95) that the energy of the ${}^1D_{xy}$ state is

$$E({}^1D_{xy}) = E_C + [x^2|y^2] + [xy|yx] \tag{100}$$

Since the energy of the ${}^1D$ states has to be the same for any value of the M_j projection (since the Hamiltonian is invariant with respect to your choice of the axis system), all the Cartesian components of the ${}^1D$ state will have the same energy. A similar invariance applies to the ${}^3P$ states. We can exploit this invariance by equating the energies given in Eqs. (98) and (100). This gives the relation

$$[x^2|x^2] - [xy|yx] = [x^2|y^2] + [xy|yx] \tag{101}$$

or

$$[x^2|x^2] = [x^2|y^2] + 2[xy|yx] \tag{102}$$

This result is reasonable. The coulomb repulsion between two electrons in the same Cartesian $2p$ will be greater than the repulsion between an electron in a $2p_x$ orbital and a 2nd electron in the $2p_y$ orbital.

Problem 20: There are three states of the C atom with $M_L = 0$ and $M_S = 0$, namely ${}^3P_{00}$, ${}^1D_{00}$, and ${}^1S_{00}$. The determinental wavefunctions for each of these states is given by Eqs. (88), (89) and (90). We wish to obtain the determinantal wavefunctions for these three states in terms of the Cartesian p spin-orbitals. To do so it is easiest to first obtain expressions for the three definite-M Slater determinants with $M_L = 0$ and M_S=0, namely

$$|p_0\bar{p}_0| = |p_z\bar{p}_z|$$

$$|p_1\bar{p}_{-1}| = -\frac{1}{2}\left(|(p_x + ip_y)(\bar{p}_x - i\bar{p}_y)|\right) = \frac{1}{2}\left(-|p_x\bar{p}_x| - |p_y\bar{p}_y| - i|p_y\bar{p}_x| + i|p_x\bar{p}_y|\right)$$

and

$$|p_{-1}\bar{p}_1| = -\frac{1}{2}\left(|(p_x - ip_y)(\bar{p}_x + i\bar{p}_y)|\right) = \frac{1}{2}\left(-|p_x\bar{p}_x| - |p_y\bar{p}_y| + i|p_y\bar{p}_x| - i|p_x\bar{p}_y|\right)$$

Consequently, for example, the wave function for the $|^3P_{00}\rangle$ state [Eq. (88)] state is

$$\left|^3P_{00}\right\rangle = \frac{1}{\sqrt{2}}\left(-|p_{-1}\bar{p}_1| + |p_1\bar{p}_{-1}|\right) = \frac{i}{\sqrt{2}}\left(|p_x\bar{p}_y| - |p_y\bar{p}_x|\right) \tag{103}$$

(a) Obtain similar equations for the $^1D_{00}$ and $^1S_{00}$ states.

(b) Then, evaluate the two-electron energy of the two $2p$ electrons in the $^3P_{00}$, $^1D_{00}$ and $^1S_{00}$ states in terms of the basic integrals $[x^2|x^2]$, $[x^2|y^2]$, and $[xy|yx]$. Remember that

$$[x^2|x^2] = [y^2|y^2] = [z^2|z^2] \tag{104}$$

$$[x^2|y^2] = [x^2|z^2] = [y^2|z^2] \text{ and so forth} \tag{105}$$

$$[xy|yx] = [xz|zy] = [yx|xy] \text{ and so forth} \tag{106}$$

and, since the electron density associated with electron 1 has different Cartesian reflection symmetry compared to the electron density associated with electron 2,

$$[xy|yz] = [xz|yz] = [zy|yx] = 0 \text{ and so forth} \tag{107}$$

To check your results, remember that all five components of the ^1D state should have the same energy, so that the expression you obtain for $\langle^1D_{x^2-y^2}|\,\hat{H}\,|^1D_{x^2-y^2}\rangle$ should equal the expression for $\langle^1D_{00}|\,\hat{H}\,|^1D_{00}\rangle$

(c) Finally, predict the relative spacing between the three valence states of an atom with a $2p^2$ configuration (such as carbon). The spacing should be similar for Si (...$3p^2$) and also for O (... $2p^4$) where there is a double hole (rather than a double occupancy) in the $2p$ shell, as well as for S (... $3p^4$). Use the NIST database to obtain the experimental spacings for C, O, Si, and S and compare these with your prediction.

6. *Simplistic description of the C atom*

This section contains a simplistic description of the C atom, free of complex orbitals. From the application of the tableau method described in Sec. IL4, we know that the $2p^2$ state of the C atom gives rise to ^3P, ^1D and ^1S electronic states. We have two electrons to distribute between the p_z, p_x, or p_y Cartesian $2p$ orbitals.

^{3}**P state**: in the triplet state we cannot have two electrons in the same orbital. Thus, the allowed electron occupancies are p_xp_y, p_xp_z, and p_yp_z. The $S=1$ Slater determinants are $|p_xp_y|$ and so on. We can designate these states at $^{3,1}P_{xy}$ and so on, where the initial superscript designates $2S+1, M_S$.

The expectation value of $1/r_{12}$ between the two $2p$ orbitals is

$$\langle ^{3,1}P_{xy}|\frac{1}{r_{12}}|^{3,1}P_{xy}\rangle = [p_x^2|p_y^2] - [p_xp_y|p_yp_x] = [x^2|y^2] - [xy|yx] \tag{108}$$

For $M_S=-1$, the determinants are $|^{3,-1}P_{xy}\rangle = |\bar{p}_x\bar{p}_y|$, with the same energy. For $M_S=0$, the determinants are

$$|^{3,0}P_{xy}\rangle = 2^{-1/2}\left[|p_x\bar{p}_y| \pm |\bar{p}_xp_y|\right] \tag{109}$$

From the rules for the energy of Slater determinants (IL3), we see that the two electron energy of the state $|^{3,0}P_{xy}\rangle$ is

$$\langle ^{3,0}P_{xy}|\frac{1}{r_{12}}|^{3,1}P_{xy}\rangle = [p_x^2|p_y^2] \pm [p_xp_y|p_yp_x] = [x^2|y^2] \pm [xy|yx] \tag{110}$$

But this has to be equal to the energy of the $^{3,1}P_{xy}$ state [Eq. (108)]. Thus, we have to take the minus sign in the definition of the $^{3,0}P_{xy}$ wavefunction. Note that you can get the same result by operating on $|^{3,1}P_{xy}\rangle$ by $\hat{S}_- = \hat{s}_{1-} + \hat{s}_{2-}$.

^{1}**S state** The electronic wavefunction in the ^1S state must be completely symmetric with respect to rotation and inversion. The first condition implies that the three Cartesian directions must be treated on an equal footing, and the second, that the Cartesian $2p$ orbitals must be doubly occupied. Thus, the wavefunction must be

$$|^1S\rangle = 3^{-1/2}\left[|x\bar{x}| + |y\bar{y}| + |z\bar{z}|\right]$$

The expectation value of $1/r_{12}$ between the two $2p$ orbitals in this state is

$$\langle {}^1S|\frac{1}{r_{12}}|{}^1S\rangle = [x^2|x^2] + 2[xy|yx] \tag{111}$$

^{1}D state The Cartesian components of the $l = 2$ spherical harmonics, also referred to as cubic harmonics are $xy, xz, yz, x^2 - y^2$ and $3z^2 - r^2$. Since $r^2 = x^2 + y^2 + z^2$, the latter is equivalent to $2z^2 - x^2 - y^2$. We thus have

$$|{}^1D_{xy}\rangle = 2^{-1/2}\left[|p_x\bar{p}_y| + |p_y\bar{p}_x|\right] \tag{112}$$

Note that imposing the "+" sign guarantees that this state is orthogonal to the $|{}^{3,0}P\rangle$ state [Eq. (110)]. Similarly we have

$$|{}^1D_{xz}\rangle = 2^{-1/2}\left[|p_x\bar{p}_z| + |p_z\bar{p}_x|\right] \tag{113}$$

$$|{}^1D_{yz}\rangle = 2^{-1/2}\left[|p_y\bar{p}_z| + |p_z\bar{p}_y|\right] \tag{114}$$

$$|{}^1D_{x^2-y^2}\rangle = 2^{-1/2}\left[|p_x\bar{p}_x| - |p_y\bar{p}_y|\right] \tag{115}$$

$$|{}^1D_{x^2-y^2}\rangle = 2^{-1/2}\left[|p_x\bar{p}_x| - |p_y\bar{p}_y|\right]$$

and, finally,

$$|{}^1D_{3z2-r^2}\rangle = |{}^1D_{z^2}\rangle = 6^{-1/2}\left[3|p_z\bar{p}_z| - |p_x\bar{p}_x| - |p_y\bar{p}_y|\right] \tag{116}$$

The expectation value of $1/r_{12}$ between the two $2p$ orbitals in the first three states is (remember that $[x^2|y^2] = [x^2|z^2] = [y^2|z^2]$ and, similarly $[xy|yx] = [xz|zx] = [yz|zy]$.

$$\langle {}^1D_{xy}|\frac{1}{r_{12}}|{}^1D_{xy}\rangle = \langle {}^1D_{xz}|\frac{1}{r_{12}}|{}^1D_{xz}\rangle = \langle {}^1D_{yz}|\frac{1}{r_{12}}|{}^1D_{yz}\rangle = [x^2|y^2] + [xy|yx] \tag{117}$$

Likewise, the expectation value of $1/r_{12}$ between the two $2p$ orbitals in the $x^2 - y^2$ and z^2 states is

$$\langle {}^1D_{x^2-y^2}|\frac{1}{r_{12}}|{}^1D_{z^2-y^2}\rangle = \langle {}^1D_{z^2}|\frac{1}{r_{12}}|{}^1D_{z^2}\rangle = [x^2|x^2] - [xy|yx] \tag{118}$$

Because of the spherical symmetry of the atom, the energies of the five components of the ${}^1D$ state must be the same. Thus, equating Eqs. (117) and(118) we obtain

$$[x^2|y^2] + [xy|yx] = [x^2|x^2] - [xy|yx]$$

or, after rearrangement

$$[x^2|x^2] = [x^2|y^2] + 2[xy|yx] \tag{119}$$

Remember that $[xy|yx]$ is the self-repulsion of the overlap amplitude between a $2p_x$ and a $2p_y$ orbital. This is a positive number. Thus, we see from the last equation that the self-repulsion between two electrons in the same $2p$ orbital is greater than the repulsion between two electrons in different $2p$ orbitals. This is physically reasonable. If we compare the expressions for the expectation value of $1/r_{12}$ between the two $2p$ orbitals in the ${}^3P$, ${}^1S$ and ${}^1D$ states [Eqs. (108), (111), and (117), and use Eq. (119) to write everything in terms of the two two-electron integrals $[x^2|y^2]$ and $[xy|yx]$ we find

$$\langle {}^3P|1/r_{12}|{}^3P\rangle = [x^2|y^2] - [xy|yx]$$

$$\langle {}^1D|1/r_{12}|{}^1D\rangle = [x^2|y^2] + [xy|yx]$$

$$\langle {}^1S|1/r_{12}|{}^1S\rangle = [x^2|y^2] + 4[xy|yx]$$

so that the relative spacing is given in Fig. 7.

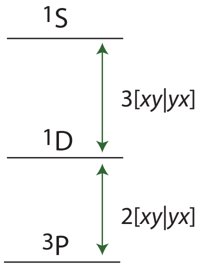

FIG. 7. Spacing between the ${}^3P$, ${}^1D$ and ${}^1S$ states of the C atom, in terms of the exchange integral $[xy|yx]$.

7. Representation of the states

The five ${}^1D$ states of the C atom [Eqs. (112)–(116)] can be thought-of as two-electron analogs of the hydrogenic $3d$ orbitals, which are shown, in their Cartesian (real) representations, in Fig. 8. For example, in the ${}^1D_{xy}$ state [Eq. (112)] there is one electron in the $2p_x$

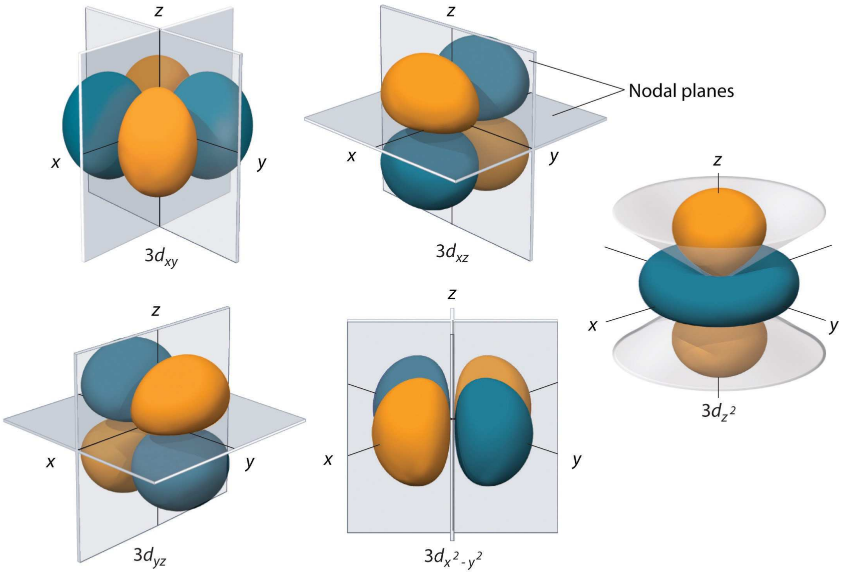

FIG. 8. Images of the Cartesian hydrogenic $3d$ orbitals, from the online version of *General Chemistry: Principles, Patterns, and Applications* by Andy Schmitz.

orbital while the other is in the $2p_y$ orbital. The numerical value of the Slater determinant $|p_x\bar{p}_y|$ is the product of a p_x orbital in the coordinates of electron 1 and a p_y orbitals in the coordinates of electron 2 (or vice-versa). This product will be large and positive when the coordinates of the two electrons (x_1, y_1, x_2 and y_2) both lie in the first and third quadrants of the x_1, y_1 and x_2, y_2 planes, large and negative, when both lie in the second and fourth quadrants of the xy plane, and small along the x or y axes. This is exactly like what is represented, qualitatively, by the upper-left-hand image in Fig. 8. The coordinate dependence of the other four Cartesian components of the ^1D state [Eqs. (113)–(116)] are illustrated similarly in Fig. 8.

8. *Reflection Symmetry*

Consider a plane containing the z and x axes. Let the operator $\hat{\sigma}_{xz}$ correspond to a reflection of all the coordinates in this plane

$$x \to x,\ y \to -y,\ z \to z$$

so that, for any function $f(x,y,z)$

$$\hat{\sigma}_{xz} f(x,y,z) = f(x,-y,z)$$

The operator corresponding to a reflection of a N-electron function is just

$$\hat{\sigma}_{xz} f(x_1, y_z, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N) = f(x_1, -y_z, z_1, x_2, -y_2, z_2, \ldots, x_N, -y_N, z_N)$$

The Hamiltonian is symmetric with respect to this operation, so that the wave functions for any state of an atom can be chosen to be eigenfunctions of this operator, either symmetric (which we label "+") or antisymmetric (which we label "–"). The Cartesian atomic orbitals are either positive (symmetric) or negative (antisymmetric). Notably, p_y is antisymmetric, while p_x and p_z are symmetric. the We see from the expression given in Eq. (103) that

$$\begin{aligned}\hat{\sigma}_{xz} \left|{}^3P_{00}\right\rangle &= \hat{\sigma}_{xz} \frac{i}{\sqrt{2}} \left(|p_x\bar{p}_y| - |p_y\bar{p}_x|\right) \\ &= \frac{i}{\sqrt{2}} \left(-|p_x\bar{p}_y| + |p_y\bar{p}_x|\right) = -\left|{}^3P_{00}\right\rangle\end{aligned}$$

so that the $|{}^3P_{00}\rangle$ state is "antisymmetric" with respect to reflection.

The definite-m p_1 and p_{-1} one-electron orbitals are neither symmetric nor antisymmetric. From their definition [Eq. (91)] we see that $\sigma_{xz} p_1 = -p_{-1}$ and $\sigma_{xz} p_{-1} = -p_1$. In three (or higher) dimensions rotations and reflections do not commute. The spherical harmonics are eigenfunctions of rotation around the z axis, and thus will not be eigenfunctions of a reflection containing the z axis. However, the overall reflection symmetry of the $|{}^3P_{00}\rangle$ state is still -1 even if we express it in terms of the definite-m orbitals [Eq. (88)], because

$$\begin{aligned}\hat{\sigma}_{xz} \left|{}^3P_{00}\right\rangle &= \hat{\sigma}_{xz} \frac{i}{\sqrt{2}} \left(-|p_{-1}\bar{p}_1| + |p_1\bar{p}_{-1}|\right) \\ &= \frac{i}{\sqrt{2}} \left(-|p_1\bar{p}_{-1}| + |p_{-1}\bar{p}_1|\right) = -\left|{}^3P_{00}\right\rangle\end{aligned}$$

Problem 21 : Determine the symmetry for reflection in the xz plane of the $|{}^1D_{00}\rangle$ and $|{}^1S_{00}\rangle$ states.

M. Spin-Orbit splitting in the C atom

The electron possesses a magnetic moment by virtue of its orbital motion

$$\vec{\mu}_l = \beta \vec{l}$$

where β is the Bohr magneton ($\beta = e\hbar/2m_e$, or, in atomic units, $\beta = 1/2$), and also by virtue of its spin

$$\vec{\mu}_s = g\beta\vec{s}$$

where the so-called "g" factor is nearly 2 (2.002319). The interaction of these two magnetic moments gives rise to the spin-orbit Hamiltonian

$$H_{so} = \sum_i a\vec{l}_i \cdot \vec{s}_i \tag{120}$$

where the sum extends over all the electrons. Here a is a constant which can be evaluated from the electronic wavefunction. There is also a term (the "spin other-orbit" term) which arises from the interaction of the spin and electronic orbital magnetic moments on two distinct electrons, but this is much smaller, so we will ignore it here.

As with any two angular momenta, you can express the dot product as

$$\vec{l}_i \cdot \vec{s}_i = l_z s_z + \frac{1}{2}\left[l_+ s_- + l_- s_+\right] \tag{121}$$

Since the spin-orbit Hamiltonian is a sum of one-electron operators, the matrix elements of H_{so} vanish between Slater determinants which differ by more than one spin-orbital. In general, for a determinant $|\psi\rangle \equiv |\phi_1\phi_2...\phi_i...\phi_N|$ we have

$$\langle\psi| H_{so} |\psi\rangle = \sum_i l_{z_i} s_{z_i} \tag{122}$$

In other words, only the $l_z s_z$ term contributes to the diagonal elements of the spin-orbit operator. Also, because s_z is alternately $+1/2$ and $-1/2$ for a doubly-filled orbital, only unfilled shells contribute. For example, in the $|{}^3P_{11}\rangle$ state [Eq. (84)], we have

$$\left\langle {}^3P_{11}\right| H_{so} \left|{}^3P_{11}\right\rangle = a\left[1\cdot\frac{1}{2}+0\cdot\frac{1}{2}\right] = \frac{1}{2}a \tag{123}$$

For two Slater determinants which differ by one spin-orbital, for example $|\psi\rangle$ [defined just before Eq. (122)] and $|\Psi\rangle \equiv |\phi_1\phi_2...\chi_i...\phi_N|$ only the $[l_+s_- + l_-s_+]$ term in Eq. (121) contributes, so that

$$\langle\Psi| H_{so} |\psi\rangle = \langle\phi_i| \frac{a}{2}\left[l_+s_- + l_-s_+\right] |\chi_i\rangle \tag{124}$$

For two Slater determinants which differ by two or more spin-orbitals, the matrix element of the spin-orbit coupling is zero.

Problem 22: For an atom with a single electron in a p orbital outside of a closed shell, as, for example, the Al atom, there are six possible states corresponding to three possible projection of the electronic orbital angular momentum $l = 1$ and the two possible projections of the spin angular momentum. The single spin-orbital corresponding to each of these six states is listed in the following table

M_L	1	1	0	0	−1	−1
M_S	1/2	−1/2	1/2	−1/2	1/2	−1/2
state	p_1	$\bar{p}_1$	p_0	$\bar{p}_0$	p_{-1}	$\bar{p}_{-1}$

a. Evaluate the matrix elements of the spin-orbit operator in the basis of the 6 ${}^2P$ states. The matrix can be written as the constant a times a matrix of numbers. Diagonalize this matrix to obtain the spin-orbit energy levels of a ${}^2P$ atom. From the NIST database determine the value of a for the B and Al atoms.

b. One can also write the total electronic orbital angular momentum ($\vec{J}$) of the atom as the vector sum of the total spin angular momentum $\vec{S}$ and the total electronic angular momentum $\vec{L}$. For an atom in a ${}^2P$ state $S = 1/2$ and $L = 1$. Thus, by the rules that applies to vector addition of two angular momentum in quantum mechanics, we see that

J=1/2 or 3/2. If you ignore the spin-other-orbit terms, show that

$$H_{so} = \sum_i a\vec{l}_i \cdot \vec{s}_i \cong A\vec{L} \cdot \vec{S}$$

Show that

$$H_{so} = \frac{1}{2}A\left(\vec{J}^2 - \vec{L}^2 - \vec{S}^2\right)$$

---

[1] The approximation is called Hartree-Fock when there are more than two electrons, so that electron exchange has to be included. For simplicity, we will designate it as Hartree-Fock even in the case of He, where there are no exchange terms.

[2] A. R. Edmonds, *Angular Momentum in Quantum Mechanics*, 2nd edition, third printing (Princeton University Press, Princeton, 1974).