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

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

where $\hat{L}^2$ is the operator for 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

$$\rho = r/a_0$$

where

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

In terms of ρ the potential becomes

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

Problem 1 : Use the chain rule

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

to show that

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

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

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

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

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

or, in terms of ρ, θ and ϕ

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

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 so-called atomic unit of distance) and the energy in units of $(4\pi\epsilon_o)^2\hbar^2/m_e e^4$ (the so-called atomic unit of energy), 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. The atomic unit of distance is called the *bohr* and the atomic unit of energy, the *hartree*.

If we multiply Eq. (2) by $2\rho^2$ and take the right hand side over to the left, we get

$$\left[-\frac{\partial}{\partial\rho}\left(r^2\frac{\partial}{\partial\rho}\right)+\hat{L}^2(\theta,\phi)-2Z\rho-2\rho^2\varepsilon\right]\psi(\rho,\theta,\phi)=0 \tag{3}$$

which we can write as

$$\left[\hat{H}_\rho(\rho)+\hat{L}^2(\theta,\phi)\right]\psi(\rho,\theta,\phi)=0 \tag{4}$$

where the definition of $\hat{H}_\rho(\rho)$ is obvious from comparison of Eqs. (3) and (4).

Here we have separated the Hamiltonian operator into a term depending only on ρ 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 ρ and a term depending only on θ and ϕ, namely

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

Inserting this into Eq. (4), dividing by ψ and simplifying we get

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

or

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

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

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

Here, the left-hand side depends only on ρ 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

$$-\frac{\hat{L}^2 Y(\theta,\phi)}{Y(\theta,\phi}) = K \tag{5}$$

and

$$\frac{\hat{H}(\rho)R(\rho)}{R(\rho)} = K \tag{6}$$

Equation (5) 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 $(j = 0, 1, 2, \ldots)$

The solutions are called Spherical Harmonics, $Y_{jm}(\theta,\phi)$; you can find expressions many places. 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. (6) as

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

or

$$\left\{ -\frac{1}{2\rho^2}\frac{\partial}{\partial\rho}\left(\rho^2\frac{\partial}{\partial\rho}\right) - \frac{Z}{\rho} + \frac{j(j+1)}{\rho^2} - \varepsilon \right\} R(\rho) = 0 \tag{7}$$

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

$$R(\rho) = G(\rho)/\rho$$

Problem 2: Show that

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

Then show that Eq. (7) reduces to

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

Equation (8) is entirely equivalent to the usual one-dimensional Schrodinger equation, with potential

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

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

The solution $G(\rho)$ 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

$$\lim_{\rho\to 0} \sim \rho^{j+1}$$

The radial functions $R(\rho)$ 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
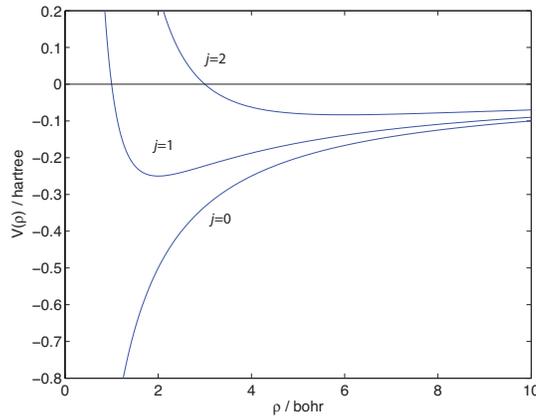
FIG. 1. $V(\rho)$ for the hydrogen atom $(Z = 1)$, with $j = 0$, 1 and 2.

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 $r^2 dr$, so that

$$\int_0^\infty R_{n',j'}(\rho)R_{n,l}(\rho)\rho^2 d\rho = \int_0^\infty G_{n',j'}(\rho)G_{n,j}(\rho)d\rho = \delta_{n,n'}\delta_{j,j'} \tag{9}$$

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

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

.

Problem 3: The radial functions for the $1s$ and $2p$ states are

$$R_{1s}(\rho) = N_{1s} \exp(-\rho Z)$$

$$R_{2p}(\rho) = N_{2p}\, \rho \exp(-\rho Z/2)$$

Use Eq. (9) to determine the two normalization coefficients N_{1s} and N_{2p}.
The radial function for the $2s$ state is

$$R_{2s}(\rho) = N_{2s}(1 + B\rho) \exp(-\rho/2Z)$$

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 ρ does the node in the $2s$ radial function occur?
Finally, 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.
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),

$$H(r,\theta,\phi) = -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \hat{L}^2(\theta,\phi)\right] + V(r) \tag{10}$$

where μ is the reduced mass of the two particles $\mu = (m_a m_b)/(m_a + m_b)$. 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 equation:

$$\left[-\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} + V(r) + \frac{\hbar^2 j(j+1)}{2\mu r^2} \right] G(r) = \mathcal{E} G(r) \tag{11}$$

C. Perturbation and Simple Variational treatment of the He atom

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

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

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

$$h(1) = -\frac{1}{2} \nabla_1^2 - Z/r_1 \tag{13}$$

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

$$H_0 = h(1) + h(2) \,. \tag{14}$$

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

$$1s = \left(\frac{Z^3}{\pi}\right)^{1/2} \exp(-Zr) \,. \tag{15}$$

The two-electron wavefunction is

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

.

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

$$
\begin{aligned}
E_0^{(1)} &= \left\langle \psi_0^{(0)}(1,2) \left| r_{12}^{-1} \right| \psi_0^{(0)}(1,2) \right\rangle \\
&= \iint 1s(1)1s(1)\frac{1}{r_{12}}1s(2)1s(2)dV_1 dV_2 \\
&= \left(\frac{Z^3}{\pi}\right)^2 \int_0^\infty r_1^2 dr_1 \int_0^\infty r_2^2 dr_2 \int_0^\pi \sin\theta_1 d\theta_1 \int_0^\pi \sin\theta_2 d\theta_2 \int_0^{2\pi} d\phi_1 \int_0^{2\pi} d\phi_2 e^{-2Zr_1}e^{-2Zr_2}r_{12}^{-1}
\end{aligned} \tag{16}
$$

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

$$\frac{1}{r_{12}} = \sum_{\lambda=0}^\infty \frac{r_<^\lambda}{r_>^{\lambda+1}} P_\lambda(\cos\theta_{12}) \tag{17}$$

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 $\lambda=0$ term in Eq. (17) will give a non-vanishing result, so when evaluating Eq. (17), you can use

$$\frac{1}{r_{12}} = \frac{1}{r_>} \tag{18}$$

Thus, schematically,

$$\iint f(r_1)\frac{1}{r_{12}}g(r_2)d\tau_1 d\tau_2 = 16\pi^2 \left[\int_0^\infty f(r_1)r_1 dr_1 \int_0^{r_1} g(r_2)r_2^2 dr_2 + \int_0^\infty g(r_2)r_2 dr_2 \int_0^{r_2} f(r_1)r_1^2 dr_1 \right] \tag{19}$$

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 $\frac{1}{r_>} = 1/r_2$. Figure 2 depicts the domain of
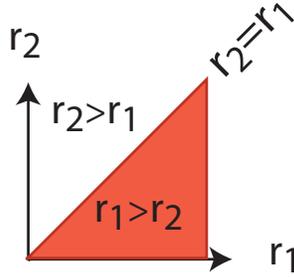
FIG. 2. Illustration of the range of integration in Eq. (19
)

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. (19).

Problem 4: Show that

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

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. From the NIST tables of electron energy levels of the atoms and positive ions we find [1] that this is 0.90357 Hartree. Thus, the total electronic energy of He is –2.90357 Hartree. The perturbation theory estimate of –2.75 is quite poor.

One improvement we can make is to introduce a variable screening constant, since each electron sees not the full nuclear charge of +2. In other words, we can define a generalized hydrogenic $1s$ orbital

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

where ζ is a variable screening constant. Then, the variational energy is

$$E_{var} = 2\langle 1s_\zeta | h | 1s_\zeta \rangle + [1s_\zeta^2 | 1s_\zeta^2]$$

Problem 5: Show that $\langle 1s_\zeta | h | 1s_\zeta \rangle = -Z\zeta + \zeta^2/2$

Problem 6: Use this result and the result of problem 5 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 7: Consider two $1s$ functions i and j, 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.

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

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

In every case, the results will be a function of both ζ and ζ'. You will first have to determine the value of the normalization constant N_i in Eq. (26). To check your method and your result know that

$$[1s^2|1s^2] \equiv [1s1s|1s1s] = \iint 1s(1)^2 \frac{1}{r_{12}} 1s(2)^2 dV_1 dV_2 = \frac{5\zeta}{8}$$

Also, for $\zeta = 1$ and $\zeta' = 3$, the values of the desired integrals are given in Table I.

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. (14) in which the zeroth-order Hamiltonian is a sum of identical one-electron terms. The best 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 [2]) approximation the Schrodinger equation for the $1s$ electron is the following one-electron, three-dimensional integro-differential equation

$$\left[-\frac{1}{2}\nabla_1^2 - \frac{2}{r_1} + \int \frac{\phi^2(r_2)}{r_{12}} d\tau_2 \right] \phi(r_1) = \varepsilon_{\text{HF}} \phi(r_1) \tag{20}$$

Since the solution appears under the integral sign, it is most straightforward to solve Eq. (20) iteratively. One guesses a solution, $\phi^{(0)}(r_1)$ determines the so-called "mean-field"

potential

$$V(r_1) = \int \frac{\phi^2(r_2)}{r_{12}} d\tau_2 \, ,$$

solves the Hartree Schroedinger equation [Eq. (20)] for $\phi^{(1)}(r_1)$, determines a new mean-field potential 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. 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. One iterates until self-consistency is reached. To illustrate this, for simplicity suppose we expand the Hartree-Fock orbital in terms of just two basis functions

$$\phi^{(n)}(r) = C_1^{(n)} \chi_1(r) + C_2^{(n)} \chi_2(r) \tag{21}$$

Here n designates the nth iteration. The averaged electron-repulsion potential is then

$$\int \frac{\phi^2(r_2)}{r_{12}} d\tau_2 = \sum_{k,l} C_k^{(n)} C_l^{(n)} \int \chi_k^*(r_2) \frac{1}{r_{12}} \chi_l(r_2) d\tau_2 \tag{22}$$

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 H in the 2×2 basis of $\{\chi_1, \chi_2\}$. Schematically, the matrix elements are sums of matrix elements of the one-electron Hamiltonian $h(1)$ (kinetic energy plus electron-nuclear potential energy) and of the mean-field repulsion $V(1)$, where

$$\mathbf{H} = h(1) + V_{12}(1) \tag{23}$$

where

$$V_{12}(1) = \int \frac{\phi^2(r_2)}{r_{12}} d\tau_2 \tag{24}$$

The matrix elements of $h(1)$ are

$$h_{kl} = -\frac{1}{2} \left\langle \chi_k \left| \nabla^2 \right| \chi_l \right\rangle - \left\langle \chi_k \left| \frac{2}{r_1} \right| \chi_l \right\rangle \tag{25}$$

We will define the basis functions $\{\chi_1, \chi_2\}$ in terms of so-called Slater (hydrogenic)

functions

$$g_i = N_i \exp(-\zeta_i r) \tag{26}$$

Note that these functions are not orthogonal, so that we will need to use one of the methods described in Subsection D of Chapter 1 to determine the variational energy.

The matrix elements of the two-electron operator $1/r_{12}$ are

$$(V_{12})_{ij} = \sum_{k,l} C_k^{(n)} C_l^{(n)} \int \chi_i^*(r_1) \chi_k^*(r_2) \frac{1}{r_{12}} \chi_j(r_1) \chi_l(r_2) d\tau_2 d\tau_1 \tag{27}$$

These so-called

$$[ij|kl] = \int \chi_i^*(r_1) \chi_k^*(r_2) \frac{1}{r_{12}} \chi_j(r_1) \chi_l(r_2) d\tau_2 d\tau_1 = \int \chi_i^*(r_1) \chi_j^*(r_1) \frac{1}{r_{12}} \chi_k(r_2) \chi_l(r_2) d\tau_2 d\tau_1 \tag{28}$$

In terms of this notation, Eq. (27) becomes

$$(V_{12})_{ij} = \sum_{k,l} C_k^{(n)} C_l^{(n)} [ij|kl] \tag{29}$$

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

$$(V_{12})_{ij} = \mathbf{c}^{(n)\,T} (h_{12})_{kl}^{ij} \, \mathbf{c}^{(n)} , \tag{30}$$

where the superscript T denotes the transpose (that is, a row vector).

Thus, the iterative procedure consists of

(a) Determination of the $N \times N$ matrix of one-electron integrals, $\mathbf{h}$

(b) Determination of the $N^2 \times N^2$ matrix of two-electron integrals $(h_{12})_{kl}^{ij}$ (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 two-electron matrix $\mathbf{V}_{12}$ from Eq. (30)

(e) Diagonalization of the $N \times N$ matrix of the Hamiltonian to determine the new coefficient vector $\mathbf{c}^{(1)}$ and the new Hartree energy $\varepsilon_{HF}^{(1)}$

(f) Iteration of steps (d) and (e) until self-consistency is reached, at which point $\mathbf{c}^{(n+1)} = c^{(n)}$

and $\varepsilon_{HF}^{(n+1)} = \varepsilon_{HF}^{(n)}$. Usually, one choses an energy cutoff criterion:

$$\left| \varepsilon_{HF}^{(n+1)} - \varepsilon_{HF}^{(n)} \right| \leq \epsilon \tag{31}$$

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

When self-consistency is reached, from Eq. (20) one sees that

$$\varepsilon_{\text{HF}} = \left\langle \phi^{(n)} \left| H_{\text{HF}} \right| \phi^{(n)} \right\rangle = \left\langle \phi^{(n)} \left| h \right| \phi^{(n)} \right\rangle + \left[\phi^{(n)} \phi^{(n)} | \phi^{(n)} \phi^{(n)} \right] \tag{32}$$

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

$$E_{\text{He}} = 2\varepsilon_{\text{HF}} - \left[\phi^{(n)} \phi^{(n)} | \phi^{(n)} \phi^{(n)} \right] . \tag{33}$$

This result is important: The variational estimate of the total energy of the atom in the Hartree-Fock approximation is not 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

$$[11|22] = [22|11]$$
$$[11|12] = [11|21] = [12|11] = [21|11]$$
$$[12|12] = [21|21] = [12|21] = [21|12]$$
$$[12|22] = [21|22] = [22|12] = [22|21]$$

Problem 8: The Matlab script double_zeta_he_scf_nonorthog.m determines the Hartree energy of a two-electron ion with nuclear charge Z and screening constants given in the array ze. The script returns, for each iteration, n (the number of the iteration), $\varepsilon_{\text{HF}}^{(n)}$ (the

Hartree energy, Eq. (20), $C_1^{(n)}$ and $C_2^{(n)}$ [the expansion coefficients in Eq. (21)], and E_{HF} (the Hartree-Fock approximation to the energy of the two-electron system. (Note that the script double_zeta_he_scf_nonorthog.m uses another script two_electron.m) Answer the following questions:

A. In the double_zeta_he_scf_nonorthog.m, the two screening constants are set to $\zeta = 1$ and $\zeta' = 3$. By varying these, determine the best (lowest) value of the Hartree-Fock approximation to the energy of the He atom.

B. In the Hartree approximation each electron moves in the average field of the other. In fact, the two electrons instantaneously avoid each other. As discussed below in Sec. I E, the the true energy of the two-electron system is lower than the Hartree energy. The difference is called the "correlation energy." Using the NIST tables of electron energy levels of the atoms and positive ions for the experimental ionization energies and the results of applying the Matlab script double_zeta_he_scf_nonorthog.m determine the correlation energies (in eV) for the two-electron ions He, Li^+, Be^{2+}, B^{3+}, C^{4+}, and Ne^{8+}.

For example, for the C^{4+} ion, you enter C IV in the NIST form, and specify `eV` in the `level units` box. After hitting `"retrieve data"`, scroll down to the entry `"C V ...  Limit"` where you find the number `64.49390`. This is the ionization potential for $\mathrm{C}^{4+} \to \mathrm{C}^{5+}+e$. You can calculate the energy of the hydrogenic C^{5+} ion using the Rydberg formula. Appropriately adding the energy of C^{5+} and the ionization potential of C^{4+} will allow you to determine the experimental energy of C^{4+}.

E.   Configuration Interaction

Expansion of the solution to the Hartree equation [Eq. (20)] 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. (26)] which are included, with the notation "double-zeta" (dz) for two functions, "triple-zeta" (tz) for three functions, etc. Table II shows the convergence of the Hartree energy for He as the number of basis functions is increased.

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

TABLE II. Convergence of calculated Hartree-Fock energies of the $1s^2$ state of the He atom.

size of basis	E_{HF} (Hartree)
double-zeta (dz)	–2.855160
triple-zeta (tz)	–2.861153
quadruple-zeta(qz)	–2.861542
quintuple-zeta (5z)	–2.861625
hextuple-zeta (6z)	–2.861673
exact [a]	-2.86168

[a] From numerical solution of Eq. (20).

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".

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

This is usually on the order of 1 eV (0.037 Hartree) for each pair of electrons. Recovery of the correlation energy can be achieved only by expanding the variational wavefunction beyond the Hartree-Fock approximation, namely (for He)

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

Here $\{\psi_m\}$ is a set of one-electron functions that are orthogonal to the Hartree-Fock 1s (ϕ_{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. 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 $\phi_{\text{HF}}\phi_2$ and one doubly-excited state ϕ_2^2. So the CI consists of 3 states. If you use a double-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 ϕ_{HF}. The CI energy is then called the sp-limit, the spd-limit, etc. Table III 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.

TABLE III. 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	$spdf$-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.

For a system with more than two electrons, the summation extends over triple, quadruple, and higher-order excitations. In practice, it is very difficult to carry out an exact CI calculation including all triple or higher-order excitations. Triple excitations can, however, be included perturbatively. Table IV compares the calculated energies for the Be atom with the exact value. The total correlation energy is 2.56 eV. 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, 8% of the correlation energy, 0.2 eV, is due to higher-order excitations, which can be included only by extremely computer-intensive calculations.

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

basis	calculation	E_{CI}	Δ_E [a]	two-electron integrals
v5z	Hartree-Fock	−14.57301	9.4×10^{-2}	5347542
v5z	CI-SD	−14.66241	4.9×10^{-3}	5347542
v5z	CC-SD(T)[b]	−14.66649	8.7×10^{-4}	5347542
exact [c]		−14.66737		

[a] $E_{calc} - E_{exact}$.
[b] Coupled-cluster calculation with perturbative inclusion of triple excitations.
[c] Sum of ionization energies.

F. Spin states of two-electron systems

In the discussion so far, we have ignored the spin of the electron. The electronic Hamiltonian [Eq. (12)] 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

$$\Psi(1, 2) = 1s(1)1s(2) \left| S(1, 2) \right\rangle. \tag{34}$$

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

$$|11\rangle = \left|\frac{1}{2}, \frac{1}{2}\right\rangle$$

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

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

Problem 9 : 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

$$|10\rangle = 2^{-1/2}\left(\left|\frac{1}{2}, \frac{-1}{2}\right\rangle + \left|\frac{-1}{2}, \frac{1}{2}\right\rangle\right) \tag{35}$$

and

$$|1 - 1\rangle = \left|\frac{-1}{2}, \frac{-1}{2}\right\rangle$$

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

$$|00\rangle = C_{1,-1}\left|\frac{1}{2}, \frac{-1}{2}\right\rangle + C_{-1,1}\left|\frac{-1}{2}, \frac{1}{2}\right\rangle \tag{36}$$

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

$$|00\rangle = 2^{-1/2}\left(\left|\frac{1}{2}, \frac{-1}{2}\right\rangle - \left|\frac{-1}{2}, \frac{1}{2}\right\rangle\right) \tag{37}$$

The electronic Hamiltonian [Eq. (12)] 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.

G.   Excited states of the He atom

Although the ground state of He must be a single, 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 single 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. (12)] in these states is

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

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 10: Consider the singlet and triplet wavefunctions for the $1s2p$ state of the He atom. Assume that the $1s$ and $2p$ functions are simple hydrogenic orbitals with screening constants ζ_s and ζ_p. Use the matrix elements given in Problem 5 and the following results

$$\left\langle 2p_{\zeta_p}\right| h \left|2p_{\zeta_p}\right\rangle = \frac{1}{2}(-Z\zeta_p + \zeta_p^2)$$

$$[1s_{\zeta_s}^2|2p_{\zeta_p}^2] = \frac{1}{32}\zeta(1 - \tau^2)(14 - 7\tau - \tau^2 + 3\tau^3 - \tau^4)$$

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

where

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

and

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

to obtain an expression for the variational energy of the $^{1(3)}1s2p$ states of He. Each of these expressions will be a function of ζ_s and ζ_p, the screening constant for the $1s$ and $2p$ orbitals.

Now, vary the screening constants to minimize the energy of the $^{1(3)}1s2p$ states. Note that the screening constants don't have to be the same for the singlet as for the triplet states.

Do the optimal screening constants agree with your guess what these should be based on considerations of the physics?

Calculate the splitting between the $1s^2$ and the $^{1(3)}1s2p$ states and between the singlet and triplet components of the $1s2p$ state. Compare your results with the experimental value of these splittings, which you can get from the NIST tables.

H. Gaussian orbitals

In application of the Hartree-Fock methodology to many-electron atoms and, especially, molecules, the calculation of the 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

$$R(r) = \sum_j C_j \exp(-\alpha_j r^2) \tag{38}$$

rather than hydrogenic (often called Slater) orbitals

$$R(r) = \sum_j C_j \exp(-\zeta_j r) \tag{39}$$

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

$$1s(r) = N \exp(-\alpha r^2) \tag{40}$$

Problem 11: Determine the value of the normalization constant, so that the Gaussian $1s$ function is normalized, namely

$$\langle 1s_\alpha | 1s_\alpha \rangle = \iiint 1s(r)^2 r^2 \sin\theta d\phi d\theta dr = 1 \tag{41}$$

Then determine an expression for the overlap integral

$$S_{\alpha'\alpha} \equiv \langle 1s(\alpha') | 1s(\alpha) \rangle = \iiint 1s'_\alpha(r) 1s_\alpha(r) r^2 \sin\theta d\phi d\theta dr \tag{42}$$

Hint: To check your work, first show that

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

You can also use the symbolic package in Matlab to evaluate the necessary integrals. For example,

$$\int_0^\infty \exp(-\alpha r^2) r^2 dr = \alpha^{-3/2} \int_0^\infty \exp(-u^2) r^2 dr$$

If you use Matlab, you will get the output

```
>> syms u
>> int(exp(-u*u)*u*u,u,0,inf)
ans = pi^(1/2)/4 >> pretty(ans)

    1/2

  PI

  -----

    4
```

To determine the energy of the H atom with a single Gaussian approximation to the $1s$ orbital, you will need to evaluate the matrix element of the one-electron Hamiltonian of Eq. (13) with $Z = 1$. For a spherical s orbital one need consider only the part of the Laplacian which involves differentiation with respect to r, namely

$$\hat{T}(\vec{r}) = \hat{T}(r) = -\frac{1}{2r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right] \tag{43}$$

You can use the symbolic algebra feature of Matlab to evaluate the derivatives, for example:

```
>> syms r
>> syms alpha
>> oness=exp(-alpha*r*r)
oness =1/exp(alpha*r^2)
>> 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 12: Obtain the analytic expression for $H_{\alpha',\alpha} \equiv \langle 1s(\alpha')|H|1s(\alpha)\rangle$ and $S_{\alpha',\alpha}$. *Hint: to check your work, S(1,1) should equal 1, S(1,3)=0.8093, H(1,1)=–0.095769 and H(1,3)=–0.0054467.* Then write a Matlab *function* script to evaluate $H_{\alpha',\alpha}$ and $S_{\alpha',\alpha}$ for arbitrary values of α and α'.

Your script for $H_{\alpha',\alpha}$ and $S_{\alpha',\alpha}$ should be of the form

```
function elts=single_gaussian_matrix_elts(alph,alphp)
...
...
...
elts=[s1s h1s];
```

where `s1s` and `h1s` are the overlap and Hamiltonian matrix elements.

Then, define a simpler function routine in which α is always equal to α', namely

```
function hmat_one=single_gaussian_matrix_elts(alph)
```

```
...

...

...

hmat_one=h1s;
```

Here, the overlap is always equal to one, since the function is normalized (You did normalize it, right?). Now that you can obtain the expectation value of the Hamiltonian for a single Gaussian function, you should be able to determine the value of α which minimizes the calculated energy. Do this first by trial and error, introducing a value, calculating the energy, and then guessing a new value and so on

```
    en=hmat_one(1);
```

Problem 13: What is the best value of α and what is the corresponding energy. Remember that the variational principle guarantees that this value should always be greater than –0.5 (in atomic units).

Then use Matlab's automatic function minimization `fminsearch` to obtain the best value

```
    emin=fminsearch('hmat_one',1)
```

which starts from an initial trial value – here 1 – and iterates until the minimum is found. Pretty cool, eh? The result you obtain should agree with the result you obtained by hand.

Let's compare the Gaussian function for the $1s$ state with the true wavefunction, which is (the following expression is normalized)

$$1s(r) = \sqrt{\frac{1}{\pi}} \exp(-r) \tag{44}$$

To plot any function it is easiest to use Matlab's `ezplot` command

```
syms r
ones=exp(-r)*sqrt(2/pi);
ezplot('ones',0,3)
```
This will plot the $1s$ orbital for $0 \leq r \leq 3$. To plot two functions on the same plot

```
syms r

ones=exp(-r)*sqrt(2/pi);
```

```
f=r*exp(-r)*sqrt(2/pi);

ezplot('ones',0,3)

hold

ezplot('f',0,3)
```

The command `hold` plots on top of a previous figure.

Problem 14: Plot your best Gaussian function compared to the true $1s$ orbital. You can label the axes by the commands `xlabel('string')` and `ylabel('string')`.

Problem 15: We will use the linear variational method to determine the best three-Gaussian approximation to the H-atom $1s$ orbital, namely

$$\phi_{1s} = \sum_{i=1}^{N} C_i N_i exp(-\alpha_i r^2) \tag{45}$$

First, you will need to write a function script, let's call it `ngauss`, that determines the energy of ϕ_{1s} given a specific choice of the three coefficients α_i. In this script, you will need to (a) set up the 3×3 overlap matrix and the 3×3 Hamiltonian matrix, then (b) diagonalize this matrix, and then (c) determine the lowest eigenvalue. When this is done, and debugged, then you will use the Matlab `fminsearch` command to find the best choice of the coefficients. To use `fminsearch`, there can be only one argument of the function `ngauss`, so that you will have to set up `ngauss` as follows (the variable `alph` is a vector containing the multiple values of the screening constant. The length of the expansion N is determined inside the function script by command `length` :

```
function energ=ngauss(alph)

n=length(alph);

% determine the matrix elements of H and S

for i=1:n

   for j=i:n

      hmat(i,j)= h(alph(i),alph(j));

      smat(i,j)= s(alph(i),alph(j));

   end

end

% fill in the lower triangle of the matrix
```

```
mat=mat+triu(mat,1)'
```

```
% then diagonalize the matrix and extract the lowest root
```

```
energ=eigs(hmat,smat)
```

Note, calculating only the upper triangle of the **H** and **S** matrix eliminates some unnecessary computer time – always an important consideration. This script involves a double nested loop (called a "do loop" in FORTRAN). Note also, that the overlap matrix is not diagonal, so you have your choice of the three diagonalization methods discussed in Subsection D of Chapter 1. Here, we have chosen the generalized eigenvalue method.

Problem 16: When your function script `ngauss` is fully debugged, then determine the best variational approximation to the energy of the H atom using three ($N = 3$) Gaussian functions, by invoking the command `fminsearch('ngauss',[alph1 alph2 alph3])` where `alph1`, `alph2`, and `alph3` are your three initial guesses. There is no guarantee that your initial guesses are a good starting point, so try with various other choices.

I.   Coupling of two angular momenta

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

$$J_\pm |jm\rangle = [j(j+1) - m(m \mp 1)]^{1/2} |j, m \pm 1\rangle.$$

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

$$|j_1 m_1 j_2 m_2\rangle \equiv |j_1 m_1\rangle |j_2 m_2\rangle$$

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 $|j_1 j_2 JM\rangle$. The two sets of eigenfunctions must be related by an orthogonal transformation, namely

$$|j_1 j_2 JM\rangle = \sum_{m_1 m_2} C_{j_1 m_1 j_2 m_2, JM} |j_1 m_1 j_2 m_2\rangle \equiv \sum_{m_1 m_2} (j_1 m_1 j_2 m_2 \,|JM) \,|j_1 m_1 j_2 m_2\rangle \qquad (46)$$

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

$$\langle j_1 j_2 J'M' \,|j_1 j_2 JM\rangle = \delta_{J,J'}\delta_{M,M'} \qquad (47)$$

and

$$\langle j_1 m_1' j_2 m_2' \,|j_1 m_2 j_2 m_2\rangle = \delta_{m_1,m_1'}\delta_{m_2,m_2'} \qquad (48)$$

These two equations, along with Eq. (46), 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. (46) 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
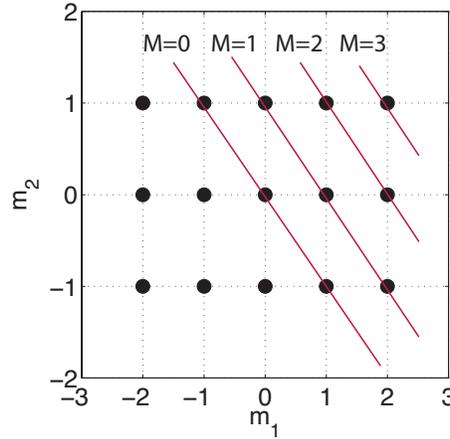

FIG. 3. Illustration of all uncoupled states for $j_1 = 2$ and $j_2 = 1$.

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.

J. 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. 3, 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. (46) reduces to

$$|j_1 j_2, J = j_1 + j_2, M = j_1 + j_2\rangle_c = (j_1, m_1 = j_1, j_2, m_2 = j_2 \,|j_1 + j_2, j_1 + j_2) \,|j_1, m_1 = j_1, j_2, m_2 = j_2\rangle_u$$

$$= (j_1 j_1 j_2 j_2 \,|j_1 + j_2, j_1 + j_2) \,|j_1 j_1, j_2 j_2\rangle_u \qquad (49)$$

Here the subscripts c and u will designate the coupled and uncoupled states. In the first line we have explicitly indicated that the projection quantum numbers m_1 and m_2 are equal to their largest values (the "stretched" values). In the second line, for notational simplicity, we have eliminated the "$m_1 = j_1$" (and so forth) terms. 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 $+1$,

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

Now, let us operate on both the left and the right hand sides of Eq. (49) with the lowering operator $J_- = j_{1-} + j_{2-}$. This gives for the operation of J_- on the coupled state (the left-hand side)

$$[J(J+1) - M(M-1)]^{1/2} \,|\, j_1 j_2, J = j_1 + j_2, M = j_1 + j_2 - 1\rangle_c$$
$$= [(j_1 + j_2)(j_1 + j_2 + 1) - (j_1 + j_2)(j_1 + j_2 - 1)]^{1/2} \,|\, j_1 j_2, J = j_1 + j_2, M = j_1 + j_2 - 1\rangle_c$$
$$= [2(j_1 + j_2)]^{1/2} \,|\, j_1 j_2, j_1 + j_2, j_1 + j_2 - 1\rangle_c \tag{50}$$

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

$$J_- \,|\, j_1 j_1 j_2 j_2\rangle_u = (j_{1-} + j_{2-}) \,|\, j_1 j_1 j_2 j_2\rangle_u$$
$$= [j_1(j_1 + 1) + j_1(j_1 - 1)]^{1/2} \,|\, j_1, j_1 - 1, j_2 j_2\rangle_u + [j_2(j_2 + 1) + j_2(j_2 - 1)]^{1/2} \,|\, j_1 j_1 j_2, j_2 - 1\rangle_u$$
$$= \sqrt{2j_1} \,|\, j_1, j_1 - 1, j_2 j_2\rangle_u + \sqrt{2j_2} \,|\, j_1 j_1 j_2, j_2 - 1\rangle_u \tag{51}$$

Equating the two previous equations gives

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

or

$$|j_1 j_2, j_1 + j_2, j_1 + j_2 - 1\rangle_c = \left[\frac{j_1}{j_1 + j_2}\right]^{1/2} |j_1, j_1 - 1, j_2 j_2\rangle_u + \left[\frac{j_2}{j_1 + j_2}\right]^{1/2} |j_1 j_1 j_2, j_2 - 1\rangle_u \tag{52}$$

The two terms on the right-hand side must be the CG coefficients as defined in Eq. (46).

Thus, we see that

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

and

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

Explicitly, in the case where $j_1 = 2$ and $j_2 = 1$ (as in Fig. 3), we have

$$\begin{aligned}
|2132\rangle_c &= (2111|32)|2111\rangle_u + (2210|32)|2210\rangle_u \\
&= (2/3)^{1/2}|2111\rangle_u + (1/3)^{1/2}|2210\rangle_u \qquad (53)
\end{aligned}$$

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. (46) reads

$$\begin{aligned}
|j_1 j_2, j_1 + j_2 - 1, j_1 + j_2 - 1\rangle_c &= (j_1 j_1 - 1 j_2 j_2 \, | \, j_1 + j_2 - 1, j_1 + j_2 - 1) \, |j_1, j_1 - 1, j_2 j_2\rangle_u \\
&\quad + (j_1 j_1 j_2 j_2 - 1 \, | \, j_1 + j_2 - 1, j_1 + j_2 - 1) \, |j_1 j_1 j_2, j_2 - 1\rangle_u (54)
\end{aligned}$$

Now, the left hand sides of Eqs. (52) and (54) 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

$$(j_1 j_1 - 1 j_2 j_2 \, | \, j_1 + j_2 - 1, j_1 + j_2 - 1) = \pm \left[\frac{j_2}{j_1 + j_2} \right]^{1/2} \qquad (55)$$

and

$$(j_1 j_1 j_2 j_2 - 1 \, | \, j_1 + j_2 - 1, j_1 + j_2 - 1) = \mp \left[\frac{j_1}{j_1 + j_2} \right]^{1/2} \qquad (56)$$

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

$$\begin{aligned}
|2122\rangle_c &= (2111|22)|2111\rangle_u + (2210|22)|2210\rangle_u \\
&= \pm(1/3)^{1/2}|2111\rangle_u \mp (2/3)^{1/2}|2210\rangle_u \qquad (57)
\end{aligned}$$

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.* [3] Consider, then, the matrix element

$$\langle 2132|\, l_{1z}\, |2122\rangle_u = \pm\frac{2^{1/2}}{3}\langle 2111|l_{1z}|2111\rangle_u \mp \frac{2^{1/2}}{3}\langle 2210|l_{1z}|2210\rangle_u$$
$$\mp\frac{2}{3}\langle 2111|l_{1z}|2210\rangle_u \pm \frac{1}{3}\langle 2210|l_{1z}|2111\rangle_u \tag{58}$$

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

$$\langle 2132|\, l_{1z}\, |2122\rangle_u = \pm\frac{2^{1/2}}{3} \mp 2\frac{2^{1/2}}{3} = \mp\frac{2^{1/2}}{3} \tag{59}$$

Consequently, for the Condon-Shortley phase convention to be satisfied we have to chose the lower sign in Eqs. (55) and (56), so that

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

and

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

Problem 17 You know that $|2133\rangle_c$ (the stretched state) $= |2211\rangle_u$. The expression for $|2132\rangle_c$ is given by Eq. (53). 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 18 For $j_1 = 2$ and $j_2 = 1$ the lowest allowed value of J is 1. In problem 17 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

$$|2111\rangle_c = a|2011\rangle_u + b|2110\rangle_u + c|221-1\rangle_u$$

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 $(1/10)^{1/2}$.

K. Slater Determinants – Atoms

For an N-electron atomic or molecular system with $N \geq 2$, the electronic wavefunction can still be expressed as a product of one-electron functions $\phi_1(\vec{r})$ ... $\phi_N(\vec{r})$. In addition to the spatial coordinates of the electron $\vec{r}$, one needs 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 $\{\varphi_1, \varphi_2, ...\varphi_{N-1}, \varphi_N\}$, 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 $\int \varphi_i^* \varphi_j dV ds = \delta_{ij}$. The Slater determinantal wavefunction for the Li atom is

$$\Psi(1,2,3) = \frac{1}{\sqrt{6}} \begin{vmatrix} 1s(1) & 1\bar{s}(1) & 2s(1) \\ 1s(2) & 1\bar{s}(2) & 2s(2) \\ 1s(3) & 1\bar{s}(3) & 2s(3) \end{vmatrix} \tag{60}$$

where $||$ denotes a determinant. The electronic Hamiltonian is

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

Show that the variational energy is given by

$$\langle \Psi(1,2,3) | H(1,2,3) | \Psi(1,2,3) \rangle = 2h_{1s} + h_{2s} + [1s1s|1s1s] + 2[1s1s|2s2s] - [1s2s|2s1s] \tag{61}$$

where

$$h_{1s} = \int 1s(1)h(1)1s(1)d\tau_1 = \int 1s(2)h(2)1s(2)d\tau_2 = \int 1s(3)h(3)1s(3)d\tau_3 \tag{62}$$

and, similarly, for h_{2s}. Also

$$[\varphi\varphi|\chi\chi] = \int\int \varphi(1)^*\varphi(1)\frac{1}{r_{12}}\chi(2)^*\chi(2)\,d\tau_1 d\tau_2 \tag{63}$$

and

$$[\varphi\chi|\chi\varphi] = \int\int \varphi(1)^*\chi(1)\frac{1}{r_{12}}\chi(2)^*\varphi(2)\,d\tau_1 d\tau_2 \tag{64}$$

Now, consider the carbon atom $(1s^2 2s^2 2p^2)$. Give the correct expression similar to Eq. (61) for the variational energy in terms of one-electron and two-electron Coulomb and exchange integrals.

In fact, the carbon atom has more than one $1s^2 2s^2 2p^2$ electronic state. From the application of the tableau method, you know that there are 15 different states, corresponding to

the 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 wavefunctions for each of these states. 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

$$\left|{}^3P_{11}\right\rangle = \frac{1}{\sqrt{6!}} \begin{vmatrix} 1s(1) & 1\bar{s}(1) & 2s(1) & 2\bar{s}(1) & 2p_1(1) & 2p_0(1) \\ 1s(2) & 1\bar{s}(2) & 2s(2) & 2\bar{s}(2) & 2p_1(2) & 2p_0(2) \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 1s(6) & 1\bar{s}(6) & 2s(6) & 2\bar{s}(6) & 2p_1(6) & 2p_0(6) \end{vmatrix} \tag{65}$$

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

$$\left|{}^3P_{11}\right\rangle = |p_1 p_0| \tag{66}$$

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. For example

$$L_- \left|{}^3P_{11}\right\rangle = (l_{1-} + l_{2-}) |p_1 p_0| \tag{67}$$

Now $l_{1-} |p_1 p_0| = 2^{1/2} |p_0 p_0|$. This vanishes, because the 5th and 6th columns of the Slater determinant are equal and any determinant vanishes if two columns are the same. However, $l_{2-} |p_1 p_0| = 2^{1/2} |p_1 p_1|$, which does not vanish. Similarly, $L_- |^3P_{11}\rangle = 2^{1/2} |^3P_{01}\rangle$. Thus, we find that

$$\left|{}^3P_{01}\right\rangle = |p_1 p_{-1}| \tag{68}$$

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: Determine the determinantal wavefunctions for the other 13 C states. Write these wavefunctions in the simplified $|p_i p_j|$ notation of Eqs. (68) and (69). The other ^3P wavefunctions can be generated, as above, by application of L_- and S_-. The ^1D wavefunc-

tions can be generated by starting with

$$\left|{}^1D_{20}\right\rangle = |p_1\bar{p}_1|$$ (69)

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 $M_S > 0$.

To help you solve this problem, several of the desired wave functions are:

$$\begin{aligned}\left|{}^3P_{00}\right\rangle = S_-\left|{}^3P_{01}\right\rangle &= (s_{1-} + s_{2-})|p_1p_{-1}| \\ &= N\left(|\bar{p}_1p_{-1}| + |p_1\bar{p}_{-1}|\right) = N\left(-|p_{-1}\bar{p}_1| + |p_1\bar{p}_{-1}|\right) \\ &= 2^{-1/2}\left(-|p_{-1}\bar{p}_1| + |p_1\bar{p}_{-1}|\right)\end{aligned}$$ (70)

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-} and s_{2-} on the right, 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 $N = 2^{-1/2}$.

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

$$\begin{aligned}\left|{}^1D_{00}\right\rangle = L_-\left|{}^1D_{10}\right\rangle &= N\left(|p_{-1}\bar{p}_1| + |p_0\bar{p}_0| + |p_0\bar{p}_0| + |p_1\bar{p}_{-1}|\right) \\ &= 6^{-1/2}\left(|p_{-1}\bar{p}_1| + |p_1\bar{p}_{-1}| + 2|p_0\bar{p}_0|\right)\end{aligned}$$ (71)

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 which have $M_S = 0$ and $M_{=}0$, namely $|p_1\bar{p}_{-1}|$, $|p_{-1}\bar{p}_1|$, and $|p_0\bar{p}_0|$,

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

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. (71) and (70). Show that the answer is

$$\left|^1S_{00}\right\rangle = 3^{-1/2}\left(|p_1\bar{p}_{-1}| + |p_{-1}\bar{p}_1| - |p_0\bar{p}_0|\right)$$

1. 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)

$$p_1 = -2^{-1/2}\left(p_x + ip_y\right) \text{ and } p_{-1} = 2^{-1/2}\left(p_x - ip_y\right) \tag{72}$$

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

$$\left|^1D_{20}\right\rangle = |p_1\bar{p}_1| = 2^{-1}\left[|p_x\bar{p}_x| - |p_y\bar{p}_y| + i\,|p_x\bar{p}_y| + i\,|p_y\bar{p}_x|\right] \tag{73}$$

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

$$\left|^1D_{-2,0}\right\rangle = |p_{-1}\bar{p}_{-1}| = 2^{-1}\left[|p_x\bar{p}_x| - |p_y\bar{p}_y| - i\,|p_x\bar{p}_y| - i\,|p_y\bar{p}_x|\right] \tag{74}$$

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

$$\left|^1D_{x^2-y^2}\right\rangle = 2^{-1/2}\left(\left|^1D_{20}\right\rangle + \left|^1D_{-2,0}\right\rangle\right) = 2^{-1/2}\left[|p_x\bar{p}_x| - |p_y\bar{p}_y|\right] = 2^{-1/2}[\,|x\bar{x}| - |y\bar{y}|\,] \tag{75}$$

and

$$\left|^1D_{xy}\right\rangle = -i2^{-1/2}\left(\left|^1D_{20}\right\rangle - \left|^1D_{-2,0}\right\rangle\right) = 2^{-1/2}\left[|p_x\bar{p}_y| + |p_y\bar{p}_x|\right] = 2^{-1/2}[\,|x\bar{y}| + |y\bar{x}|\,] \tag{76}$$

In the appendix on Slater determinants, I give a formula for the energy of a Slater determinant with spin-orbitals ϕ_1, ϕ_2, $\cdots$, ϕ_N occupied, namely, if

$$\Psi = |\phi_1\phi_2\cdots\phi_N| \tag{77}$$

then

$$\langle \Psi | H | \Psi \rangle = \sum_{i=1}^{N} \varepsilon_{\phi_i} + \sum_{i} \sum_{j>i} \left[\phi_i^2 | \phi_j^2 \right] - \delta_{\sigma_i, \sigma_j} \sum_{i} \sum_{j>i} [\phi_i \phi_j | \phi_j \phi_i] \tag{78}$$

Here

$$\varepsilon_{\phi_i} = \langle \phi_i | h | \phi_i \rangle \ , \tag{79}$$

$$\left[\phi_i^2 | \phi_j^2 \right] = \int\!\!\int \phi_i^*(1)\phi_i(1)\frac{1}{r_{12}}\phi_j^*(2)\phi_j(2)d\tau_1 d\tau_2 \tag{80}$$

and

$$[\phi_i \phi_j | \phi_j \phi_i] = \int\!\!\int \phi_i^*(1)\phi_j(1)\frac{1}{r_{12}}\phi_j^*(2)\phi_i(2)d\tau_1 d\tau_2 \tag{81}$$

Thus, the energy of the $^1D_{x^2-y^2}$ state is

$$E(^1D_{x^2-y^2}) = 2\varepsilon_{1s} + 2\varepsilon_{2s} + 2\varepsilon_{2p} + [1s^2|1s^2] + [2s^2|2s^2] + 4[1s^2|2s^2] + 2[1s^2|2p_x^2] + 2[2s^2|2p_x^2]$$
$$-2[1s2s|2s1s] - 2[1s2p_x|2p_x1s] - 2[2s2p_x|2p_x2s]$$
$$+[2p_x^2|2p_x^2] - [2p_x2p_y|2p_y2p_x] \tag{82}$$

Note that, because an s orbital is spherically symmetric,

$$[s^2|2p_x^2] = [s^2|2p_y^2] \tag{83}$$

and

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

and

$$[s2p_x|2p_ys] = 0$$

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. (82) to read

$$E(^1D_{x^2-y^2}) = E_C + [2p_x^2|2p_x^2] - [2p_x2p_y|2p_y2p_x] = E_C + [x^2|x^2] - [xy|yx] \tag{84}$$

where

$$E_C = 2\varepsilon_{1s} + 2\varepsilon_{2s} + 2\varepsilon_{2p} + [1s^2|1s^2] + [2s^2|2s^2] + 4[1s^2|2s^2] + 2[1s^2|2p_x^2] + 2[2s^2|2p_x^2]$$

$$-2[1s2s|2s1s] - 2[1s2p_x|2p_x1s] - 2[2s2p_x|2p_x2s] \tag{85}$$

We see from Eq. (84) 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. (76) that the energy of the $^1D_{xy}$ state is

$$E(^1D_{xy}) = E_C + [x^2|y^2] + [xy|yx] \tag{86}$$

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. (84) and (86). This gives the relation

$$[x^2|x^2] - [xy|yx] = [x^2|y^2] + [xy|yx] \tag{87}$$

or

$$[x^2|x^2] = [x^2|y^2] + 2[xy|yx] \tag{88}$$

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: Determine the determinantal wavefunctions for the C states with $M_L = 0$ and $M_S=0$ in terms of the Cartesian p spin-orbitals. To obtain these results, 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. (70)] state is

$$\left|^3P_{00}\right\rangle = \frac{1}{\sqrt{2}}\left(-|p_{-1}\bar{p}_1| + |p_1\bar{p}_{-1}|\right) = \frac{i}{\sqrt{2}}\left(|p_x\bar{p}_y| - |p_y\bar{p}_x|\right) \qquad (89)$$

Then, evaluate the two-electron energy of the two $2p$ electrons in each of these states in terms of the basis integrals $[x^2|x^2]$, $[x^2|y^2]$, and $[xy|yx]$. Remember that

$$[x^2|x^2] = [y^2|y^2] = [z^2|z^2] \qquad (90)$$

$$[x^2|y^2] = [x^2|z^2] = [y^2|z^2] \text{ and so forth} \qquad (91)$$

$$[xy|yx] = [xz|zx] = [yx|xy] \text{ and so forth} \qquad (92)$$

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

$$[xy|yz] = [xz|yz] = [zy|yx] = 0 \text{ and so forth} \qquad (93)$$

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 $\langle^1D_{00}|\,\hat{H}\,|^1D_{00}\rangle$

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.

2. 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

$$x \rightarrow x, \ y \rightarrow -y, \ z \rightarrow z$$

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. (89) that

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

so that the $\left|^3 P_{00}\right\rangle$ 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. (72)] 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 $\left|^3 P_{00}\right\rangle$ state is still -1 even if we express it in terms of the definite-m orbitals [Eq. (70)], because

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

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

L.   Spin-Orbit coupling

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

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

where β is the Bohr magneton ($\beta = ...$), and also by virtue of its spin

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

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

$$H_{so} = \sum_i a\vec{l}_i \cdot \vec{s}_i \tag{94}$$

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 that we will ignore it here.

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

$$\vec{l} \cdot \vec{s} = l_z s_z + \frac{1}{2} [l_+ s_- + l_- s_+] \tag{95}$$

Problem 22 : Prove Eq. (95).

Suppose that the wave functions for each state are expressed as a sum of Slater determinants. Each spin-orbital is an eigenfunction of both l_z and s_z (in the latter case the eigenvalue is $\pm 1/2$). Thus the action of $\sum l_{z_i} s_{z_i}$ on a given Slater determinant is a constant times the same Slater determinant, namely

$$\sum_i l_{z_i} s_{z_i} |\phi_1 \phi_2 ... \phi_i ... \phi_N| = C |\phi_1 \phi_2 ... \phi_i ... \phi_N|$$

Consequently, the matrix of the operator $\sum l_{z_i} s_{z_i}$ is diagonal.

Also, since the effect of l_+s_- or l_-s_+ is to raise m_l while simultaneously lowering m_s (or vice versa), the effect of $\sum l_{z_i}s_{z_i}$ on a given Slater determinant is to yield either zero (if the raising or lowering operators operate on an orbital for which m_l or m_s is at the the top (or bottom) of their allowable range, or to yield a Slater determinant in which the the value of the sum of $m_l + m_s$ is unchanged.

Since the spin-orbit Hamiltonian is a sum of one-electron operators, the matrix elements of $\hat{H}_{so}$ 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

$$\langle\psi|\,H_{so}\,|\psi\rangle = \sum_i l_{z_i}s_{z_i} \tag{96}$$

In other words, only the l_zs_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, consider the six states which correspond to a p^1 electron occupancy (the B atom, say). We can label these states p_1, $\bar{p}_1$, p_0, $\bar{p}_0$, p_{-1}, and $\bar{p}_{-1}$. The diagonal matrix of l_zs_z is (there is only one electron to consider, so there is no sum over i)

$$\begin{pmatrix}
 & p_1 & \bar{p}_1 & p_0 & \bar{p}_0 & p_{-1} & \bar{p}_{-1} \\
\hline
p_1 & 1/2 & 0 & 0 & 0 & 0 & 0 \\
\bar{p}_1 & 0 & -1/2 & 0 & 0 & 0 & 0 \\
p_0 & 0 & 0 & 0 & 0 & 0 & 0 \\
\bar{p}_0 & 0 & 0 & 0 & 0 & 0 & 0 \\
p_{-1} & 0 & 0 & 0 & 0 & -1/2 & 0 \\
\bar{p}_{-1} & 0 & 0 & 0 & 0 & 0 & 1/2
\end{pmatrix} \tag{97}$$

As discussed in the paragraph before Eq. (96), only the l_+s_- or l_-s_+ terms result in off-diagonal coupling. there is no coupling between terms for which the sum of m_l and m_s is unchanged. Thus, for example

$$\langle p_1|\,\hat{H}_{so}\,|\bar{p}_0\rangle = a/2\,\langle p_1|\,l_+s_- + l_-s_+\,|\bar{p}_0\rangle = a/2\langle p_1\,|p_{-1}\rangle = 0$$

and

$$\langle \bar{p}_1 | \hat{H}_{so} | p_0 \rangle = a/2 \langle \bar{p}_1 | l_+ s_- + l_- s_+ | p_0 \rangle = a/2 \langle \bar{p}_1 | \bar{p}_1 \rangle = 1/2$$

Note that in the first case $m_l + m_s$ is $3/2$ for the bra and $-1/2$ for the ket, so that the matrix element vanishes. In the second case, $m_l + m_s = 1/2$ for the bra and $1/2$ for the ket, so that the matrix element of $\hat{H}_{so}$ is non-vanishing.

Problem 23 : Evaluate all the other off-diagonal matrix elements of the spin-orbit operator in the basis of the six p^1 states. Add this matrix to the diagonal component [Eq. (97)], then diagonalize this to get the spin-orbit energies.

Answer

$$\begin{pmatrix} & p_1 & \bar{p}_1 & p_0 & \bar{p}_0 & p_{-1} & \bar{p}_{-1} \\ p_1 & 1/2 & 0 & 0 & 0 & 0 & 0 \\ \bar{p}_1 & 0 & -1/2 & -2^{-1/2} & 0 & 0 & 0 \\ p_0 & 0 & -2^{-1/2} & 0 & 0 & 0 & 0 \\ \bar{p}_0 & 0 & 0 & 0 & 0 & -2^{-1/2} & 0 \\ p_{-1} & 0 & 0 & 0 & -2^{-1/2} & -1/2 & 0 \\ \bar{p}_{-1} & 0 & 0 & 0 & 0 & 0 & 1/2 \end{pmatrix}$$

Note that this 6×6 matrix factors into two uncoupled 3×3 matrices, which have identical eigenvalues. This identity between the two 3×3 matrices is easier to see if we rearrange the states as follows:

$$\begin{pmatrix} & p_1 & p_0 & \bar{p}_1 & \bar{p}_{-1} & \bar{p}_0 & p_{-1} \\ p_1 & 1/2 & 0 & 0 & 0 & 0 & 0 \\ p_0 & 0 & 0 & -2^{-1/2} & 0 & 0 & 0 \\ \bar{p}_1 & 0 & -2^{-1/2} & -1/2 & 0 & 0 & 0 \\ \bar{p}_{-1} & 0 & 0 & 0 & 1/2 & 0 & 0 \\ \bar{p}_0 & 0 & 0 & 0 & 0 & 0 & -2^{-1/2} \\ p_{-1} & 0 & 0 & 0 & 0 & -2^{-1/2} & -1/2 \end{pmatrix}$$

Problem 24 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

$$H_{so} = a \sum_i \vec{l_i} \cdot \vec{s_i} \cong a\vec{L} \cdot \vec{S}$$

Then show that

$$\hat{H}_{so} = \frac{a}{2} \left(\hat{J}^2 - \hat{L}^2 - \hat{S}^2 \right)$$

Use this expression to evaluate the spin-orbit energies and degeneracies of the spin-orbit states of an atom in a p^1 (^2P) and a p^2 (^3P) state. The first answer should agree with what you obtained in Problem 23.

M.   Time reversal states

Under the effect of time reversal, the projection of angular momentum states changes sign. Specifically, if $\boldsymbol{\theta}$ is the time-reversal operator, then[4]

$$\boldsymbol{\theta} \, |jm\rangle = (-1)^{j-m} \, |j - m\rangle$$

Or, $\boldsymbol{\theta}|1m\rangle = -(-1)^m|1 - m\rangle$ and $\boldsymbol{\theta}|1/2, \pm 1/2\rangle = \pm|1/2, \mp 1/2\rangle$, so that

$$\boldsymbol{\theta} p_0 = -\bar{p}_0$$

$$\boldsymbol{\theta} \bar{p}_0 = +p_0$$

$$\boldsymbol{\theta} p_1 = \bar{p}_{-1}$$

$$\boldsymbol{\theta} \bar{p}_1 = -p_{-1}$$

$$\boldsymbol{\theta} p_{-1} = \bar{p}_1$$

and

$$\boldsymbol{\theta} \bar{p}_{-1} = -p_1$$

Thus, proper time-reversal invariant states are

$$|0_\pm\rangle = 2^{-1/2} \left(p_0 \pm i\bar{p}_0 \right)$$

$$|3/2_\pm\rangle = 2^{-1/2} \left(p_1 \pm i\bar{p}_{-1} \right)$$

and

$$|1/2_\pm\rangle = 2^{-1/2} \left(\bar{p}_1 \mp i p_{-1} \right)$$

Here we designate the linear combinations of the $m_l = 1$ and -1 states by the absolute value of $\omega = m_l + m_s$.

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[1] Retrieve the data for He I, then scroll down until you find `He II (2S1/2) Limit 198 310.669`. This is the ionization potential of He.

[2] 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.

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

[4] D. M. Brink and G. R. Satchler, *Angular Momentum*, 2nd edition (Clarendon Press, Oxford, 1974) p. 62.