

# Mid-Term Examination 1

Chemistry 3BB3; Winter 2003

## Part 1. “Thinking Problems” (45 points)

Don't let yourself get frustrated on these. If you find something you can't work, move on. (These are not in increasing order of difficulty or anything like that.)

### 1. Hermitian Operators.

In this problem you will derive some properties of Hermitian operators. First, recall that a Hermitian operator is defined as one which satisfies

$$\begin{aligned}\int \Psi^*(\tau) \hat{Q} \Psi(\tau) d\tau &= \int (\hat{Q} \Psi(\tau))^* \Psi(\tau) d\tau \\ &= \int \Psi(\tau) (\hat{Q} \Psi(\tau))^* d\tau \\ &= \int \Psi(\tau) (\hat{Q}^* \Psi^*(\tau)) d\tau\end{aligned}\tag{1}$$

for an choice of wave function,  $\Psi(\tau)$ . Here,  $\tau$  is a shorthand for the variables of integration, whatever they may be.

- a. Suppose that Eq. (1) holds, and that  $\Psi(\tau)$  is an eigenfunction of  $\hat{Q}$  with eigenvalue  $q$ . That is,

$$\hat{Q} \Psi(\tau) = q \Psi(\tau)\tag{2}$$

Show that  $q$  must be a real number.

Hint:  $q$  can always be broken up into a sum of its real and imaginary parts,  $q = a + bi$  where  $a$  and  $b$  are real. Thus,  $q = q^*$ , then  $q = a + bi = a - bi = q^*$ , so  $b = 0$  and  $q$  is real.

Substituting Eq. (2), we have that

$$\begin{aligned}\int \Psi^*(\tau) \hat{Q} \Psi(\tau) d\tau &= \int \Psi^*(\tau) q \Psi(\tau) d\tau = q \int \Psi^*(\tau) \Psi(\tau) d\tau \\ \int (\hat{Q} \Psi(\tau))^* \Psi(\tau) d\tau &= \int (q \Psi(\tau))^* \Psi(\tau) d\tau = q^* \int \Psi^*(\tau) \Psi(\tau) d\tau\end{aligned}$$

Then, using Eq. (1), we see that the first expressions on the first and second lines are equivalent. Thus, the last two expressions on the first and second lines are also equivalent. This implies that  $q = q^*$  and, according to the “hint”, this indicates that  $q$  is real.

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- b. Suppose that the eigenvalues of  $\hat{Q}$  are real. Show that  $\hat{Q}$  must be Hermitian. That is, show that if all the eigenvalues of  $\hat{Q}$  are real, then Eq. (1) must be true.

Hint: Use the fact that any wave function can be expanded in terms of the eigenfunctions of  $\hat{Q}$ ,

$$\Psi(\tau) = \sum_k c_k \varphi_k(\tau) \quad (3)$$

where

$$\hat{Q}\varphi_k(\tau) = q_k \varphi_k(\tau). \quad (4)$$

Substitute Eq. (3) into the first expression in Eq. (1)

$$\begin{aligned} \int \Psi^*(\tau) \hat{Q} \Psi(\tau) d\tau &= \int \left( \sum_k c_k^* \varphi_k^*(\tau) \right) \hat{Q} \left( \sum_j c_j \varphi_j(\tau) \right) d\tau \\ &= \sum_j \sum_k c_j^* c_k \int \varphi_k^*(\tau) \hat{Q} \varphi_j(\tau) d\tau \\ &= \sum_j \sum_k c_j^* c_k \int \varphi_k^*(\tau) q_j \varphi_j(\tau) d\tau \\ &= \sum_j \sum_k c_j^* c_k q_j \int \varphi_k^*(\tau) \varphi_j(\tau) d\tau \end{aligned}$$

However,  $\int \varphi_k^*(\tau) \varphi_j(\tau) d\tau = 0$  unless  $j = k$  (and  $\int \varphi_k^*(\tau) \varphi_k(\tau) d\tau = 1$  since the wave functions are normalized), so

$$\begin{aligned} \int \Psi^*(\tau) \hat{Q} \Psi(\tau) d\tau &= \sum_j \sum_k c_j^* c_k q_j \int \varphi_k^*(\tau) \varphi_j(\tau) d\tau \\ &= \sum_j \sum_k c_j^* c_k q_j \delta_{kj} \\ &= \sum_k c_k^* c_k q_k \\ &= \sum_k |c_k|^2 q_k. \end{aligned}$$

Similarly, the second expression in Eq. (1) can be written as

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$$\begin{aligned}
\int \left( \hat{Q} \Psi(\tau) \right)^* \Psi(\tau) d\tau &= \int \left( \hat{Q} \sum_k c_k \varphi_k(\tau) \right)^* \left( \sum_j c_j \varphi_j(\tau) \right) d\tau \\
&= \int \left( \sum_k c_k \hat{Q} \varphi_k(\tau) \right)^* \left( \sum_j c_j \varphi_j(\tau) \right) d\tau \\
&= \int \left( \sum_k c_k^* q_k^* \varphi_k^*(\tau) \right) \left( \sum_j c_j \varphi_j(\tau) \right) d\tau \\
&= \sum_k \sum_j c_k^* c_j q_k^* \int \varphi_k^*(\tau) \varphi_j(\tau) d\tau \\
&= \sum_k \sum_j c_k^* c_j q_k^* \delta_{kj} \\
&= \sum_k c_k^* c_k q_k^* \\
&= \sum_k |c_k|^2 q_k^*
\end{aligned}$$

but since the eigenvalues are real,  $q_k^* = q_k$  and

$$\int \left( \hat{Q} \Psi(\tau) \right)^* \Psi(\tau) d\tau = \sum_k |c_k|^2 q_k$$

which is the same result we obtained two equations before for  $\int \Psi^*(\tau) \hat{Q} \Psi(\tau) d\tau$ . Clearly, then if the eigenvalues are all real, then

$$\int \Psi^*(\tau) \hat{Q} \Psi(\tau) d\tau = \sum_k |c_k|^2 q_k = \int \left( \hat{Q} \Psi(\tau) \right)^* \Psi(\tau) d\tau.$$

Together, parts **a** and **b** show that an operator is Hermitian if and only if it has real eigenvalues. Non-Hermitian operators will *always* have at least one non-real eigenvalue.

**c.** Show that if Eq. (1) is true, then

$$\int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau = \int \left( \hat{Q} \Phi(\tau) \right)^* \Psi(\tau) d\tau \quad (5)$$

In this case,  $\Phi(\tau)$  and  $\Psi(\tau)$  are *not* the same wave function.

We start with the definition, Eq. (1) but this time we choose the wave function to be  $\Psi(\tau) + c\Phi(\tau)$  where  $c$  is a complex number,  $c = a + bi$ .

$$\begin{aligned}
\int (\Psi(\tau) + c\Phi(\tau))^* \hat{Q} (\Psi(\tau) + c\Phi(\tau)) d\tau &= \int \left( \hat{Q} (\Psi(\tau) + c\Phi(\tau)) \right)^* (\Psi(\tau) + c\Phi(\tau)) d\tau \\
\int \Psi^*(\tau) \hat{Q} \Psi(\tau) d\tau + c^* \int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau + c \int \Psi^*(\tau) \hat{Q} \Phi(\tau) d\tau + |c|^2 \int \Phi^*(\tau) \hat{Q} \Phi(\tau) d\tau \\
&= \int \left( \hat{Q} \Psi(\tau) \right)^* \Psi(\tau) d\tau + c^* \int \left( \hat{Q} \Phi(\tau) \right)^* \Psi(\tau) d\tau + c \int \left( \hat{Q} \Psi(\tau) \right)^* \Phi(\tau) d\tau \\
&\quad + |c|^2 \int \left( \hat{Q} \Phi(\tau) \right)^* \Phi(\tau) d\tau
\end{aligned}$$

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Because  $\hat{Q}$  is Hermitian, we can use Eq. (1) to simplify the RHS of the equality, obtaining

$$\begin{aligned} & \int \Psi(\tau)^* \hat{Q} \Psi(\tau) d\tau + c^* \int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau + c \int \Psi^*(\tau) \hat{Q} \Phi(\tau) d\tau + |c|^2 \int \Phi^*(\tau) \hat{Q} \Phi(\tau) d\tau \\ &= \int \Psi(\tau)^* \hat{Q} \Psi(\tau) d\tau + c^* \int (\hat{Q} \Phi(\tau))^* \Psi(\tau) d\tau + c \int (\hat{Q} \Psi(\tau))^* \Phi(\tau) d\tau \\ & \quad + |c|^2 \int \Phi^*(\tau) \hat{Q} \Phi(\tau) d\tau \end{aligned}$$

Thus,

$$\begin{aligned} & c^* \int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau + c \int \Psi^*(\tau) \hat{Q} \Phi(\tau) d\tau = c^* \int (\hat{Q} \Phi(\tau))^* \Psi(\tau) d\tau + c \int (\hat{Q} \Psi(\tau))^* \Phi(\tau) d\tau \\ & c^* \left( \int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau - \int (\hat{Q} \Phi(\tau))^* \Psi(\tau) d\tau \right) + c \left( \int \Psi^*(\tau) \hat{Q} \Phi(\tau) d\tau - \int (\hat{Q} \Psi(\tau))^* \Phi(\tau) d\tau \right) = 0 \end{aligned}$$

A mathematician would instantly recognize that the coefficients of  $c$  and  $c^*$  must both be zero. That the coefficient of  $c^*$  must be zero gives Eq. (5), while the coefficient of  $c$  being zero gives an equation like Eq. (5), but with the roles of  $\Psi(\tau)$  and  $\Phi(\tau)$  interchanged.

If the preceding equation is not enough to convince you of the validity of Eq. (5), write  $c = a + bi$ . Then, we must have that both the real part and the imaginary parts of the equation are zero. Ergo,

$$\begin{aligned} & \text{Re} \left[ c^* \left( \int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau - \int (\hat{Q} \Phi(\tau))^* \Psi(\tau) d\tau \right) + c \left( \int \Psi^*(\tau) \hat{Q} \Phi(\tau) d\tau - \int (\hat{Q} \Psi(\tau))^* \Phi(\tau) d\tau \right) \right] = 0 \\ & \text{Im} \left[ c^* \left( \int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau - \int (\hat{Q} \Phi(\tau))^* \Psi(\tau) d\tau \right) + c \left( \int \Psi^*(\tau) \hat{Q} \Phi(\tau) d\tau - \int (\hat{Q} \Psi(\tau))^* \Phi(\tau) d\tau \right) \right] = 0 \end{aligned}$$

Substituting for  $c$  gives

$$\begin{aligned} & a \left[ \left( \int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau - \int (\hat{Q} \Phi(\tau))^* \Psi(\tau) d\tau \right) + \left( \int \Psi^*(\tau) \hat{Q} \Phi(\tau) d\tau - \int (\hat{Q} \Psi(\tau))^* \Phi(\tau) d\tau \right) \right] = 0 \\ & b \left[ \left( \int \Psi^*(\tau) \hat{Q} \Phi(\tau) d\tau - \int (\hat{Q} \Psi(\tau))^* \Phi(\tau) d\tau \right) - \left( \int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau - \int (\hat{Q} \Phi(\tau))^* \Psi(\tau) d\tau \right) \right] = 0 \end{aligned}$$

and so

$$\begin{aligned} & \left[ \left( \int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau - \int (\hat{Q} \Phi(\tau))^* \Psi(\tau) d\tau \right) + \left( \int \Psi^*(\tau) \hat{Q} \Phi(\tau) d\tau - \int (\hat{Q} \Psi(\tau))^* \Phi(\tau) d\tau \right) \right] = 0 \\ & \left[ \left( \int \Psi^*(\tau) \hat{Q} \Phi(\tau) d\tau - \int (\hat{Q} \Psi(\tau))^* \Phi(\tau) d\tau \right) - \left( \int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau - \int (\hat{Q} \Phi(\tau))^* \Psi(\tau) d\tau \right) \right] = 0 \end{aligned}$$

Taking the first equation and subtracting the second equation gives

$$2 \left( \int \Phi^*(\tau) \hat{Q} \Psi(\tau) d\tau - \int (\hat{Q} \Phi(\tau))^* \Psi(\tau) d\tau \right) = 0$$

which implies Eq. (5).

## 2. Generalizations of the Hellmann-Feynman Theorem

In this problem we will consider two generalizations of the Hellmann-Feynman theorem. Recall that the Hellmann-Feynman theorem tells us how the energy changes when we change a parameter in the Hamiltonian by a very small amount. The following theorems generalize this result and describe how the energy changes when we change the Hamiltonian by a larger amount.

**Integrated Hellmann-Feynman Theorem:** Suppose the Hamiltonian,  $\hat{H}(\lambda)$ , depends on some parameter  $\lambda$ .

Let  $\Psi(\lambda)$  be an eigenfunction of  $\hat{H}(\lambda)$ ,

$$\hat{H}(\lambda)\Psi(\lambda) = E(\lambda)\Psi(\lambda) \quad (6)$$

Then

$$E(\lambda_2) - E(\lambda_1) = \int_{\lambda_1}^{\lambda_2} \left\langle \Psi(\mu) \left| \left( \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right) \right|_{\lambda=\mu} \right| \Psi(\mu) \right\rangle d\mu. \quad (7)$$

where  $\left( \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right)_{\lambda=\mu}$  denotes the derivative of the Hamiltonian with respect to  $\lambda$  at the value  $\lambda = \mu$ .

**Integral Hellmann-Feynman Theorem:** Suppose that the Hamiltonian,  $\hat{H}(\lambda)$ , depends on some parameter  $\lambda$ . Let  $\Psi(\lambda)$  be an eigenfunction of  $\hat{H}(\lambda)$ , satisfying Eq. (6). Then

$$E(\lambda_2) - E(\lambda_1) = \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \quad (8)$$

a. Derive the Integrated Hellmann-Feynman theorem.

The Hellmann-Feynman theorem says that

$$\left. \frac{\partial E(\lambda)}{\partial \lambda} \right|_{\lambda=\mu} = \left\langle \Psi(\mu) \left| \left( \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right) \right|_{\lambda=\mu} \right| \Psi(\mu) \right\rangle$$

Substituting this into Eq. (7), we have that

$$\int_{\lambda_1}^{\lambda_2} \left\langle \Psi(\mu) \left| \left( \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right) \right|_{\lambda=\mu} \right| \Psi(\mu) \right\rangle d\mu = \int_{\lambda_1}^{\lambda_2} \left. \frac{\partial E(\lambda)}{\partial \lambda} \right|_{\lambda=\mu} d\mu.$$

Applying the fundamental theorem of calculus to the right-hand-side of this equation gives Eq. (7).

**b. Derive the Integral Hellmann-Feynman theorem.**

Starting with Eq. (8), we have that

$$\begin{aligned} \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} &= \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} - \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \\ &= \frac{\langle \hat{H}(\lambda_2) \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} - \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_1) \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}. \end{aligned}$$

In the second line we use the fact that the Hamiltonian is a Hermitian operator, so that Eq. (5) holds. Using the fact that  $\Psi(\lambda_{1,2})$  is an eigenfunction of  $\hat{H}(\lambda_{1,2})$  with eigenvalue  $E(\lambda_{1,2})$ , we have that

$$\begin{aligned} \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} &= \frac{\langle \hat{H}(\lambda_2) \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} - \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_1) \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \\ &= \frac{\langle E(\lambda_2) \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} - \frac{\langle \Psi(\lambda_2) | E(\lambda_1) \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \\ &= E(\lambda_2) \frac{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} - E(\lambda_1) \frac{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \\ &= E(\lambda_2) - E(\lambda_1) \end{aligned}$$

which completes the proof.

**c. Evaluate the following expression:**

$$\frac{\int_0^\infty e^{-\left(\frac{Zn' + Z'n}{nn'}\right)r} L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right) L_{n'-l-1}^{2l+1}\left(\frac{2Z'r}{n'}\right) r^{2l+1} dr}{\int_0^\infty e^{-\left(\frac{Zn' + Z'n}{nn'}\right)r} L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right) L_{n'-l-1}^{2l+1}\left(\frac{2Z'r}{n'}\right) r^{2l+2} dr} \quad (9)$$

Hint: The Hydrogenic orbitals for a one-electron atom with atomic number  $Z$  can be written as

$$\Psi_{n,l,m}^{(Z)}(r, \theta, \phi) = \sqrt{\left(\frac{2Z}{n}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} \left(\frac{2Zr}{n}\right)^l L_{n-(l+1)}^{2l+1}\left(\frac{2Zr}{n}\right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi) \quad (10)$$

Rewrite Eq. (10) as

$$\Psi_{n,l,m}^{(Z)}(r, \theta, \phi) = N_{n,l}^{(Z)} r^l L_{n-(l+1)}^{2l+1}\left(\frac{2Zr}{n}\right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi)$$

where  $N_{n,l}^{(Z)}$  is the normalization constant.

Consider the one-electron atoms with atomic numbers  $Z$  and  $Z'$ . We have that

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$$\begin{aligned}
 E_{n',l,m}(Z') - E_{n,l,m}(Z) &= \frac{\langle \Psi_{n,l,m}^{(Z')} (r, \theta, \phi) | \hat{H}(Z') - \hat{H}(Z) | \Psi_{n,l,m}^{(Z)} (r, \theta, \phi) \rangle}{\langle \Psi_{n,l,m}^{(Z')} (r, \theta, \phi) | \Psi_{n,l,m}^{(Z)} (r, \theta, \phi) \rangle} \\
 \frac{-(Z')^2}{2(n')^2} + \frac{Z^2}{2n^2} &= \frac{\langle \Psi_{n',l,m}^{(Z')} (r, \theta, \phi) | \frac{-Z'}{r} - \frac{-Z}{r} | \Psi_{n,l,m}^{(Z)} (r, \theta, \phi) \rangle}{\langle \Psi_{n',l,m}^{(Z')} (r, \theta, \phi) | \Psi_{n,l,m}^{(Z)} (r, \theta, \phi) \rangle} \\
 \frac{-(Z')^2}{2(n')^2} + \frac{Z^2}{2n^2} &= (Z - Z') \frac{\langle \Psi_{n',l,m}^{(Z')} (r, \theta, \phi) | \frac{1}{r} | \Psi_{n,l,m}^{(Z)} (r, \theta, \phi) \rangle}{\langle \Psi_{n',l,m}^{(Z')} (r, \theta, \phi) | \Psi_{n,l,m}^{(Z)} (r, \theta, \phi) \rangle} \\
 \frac{(Zn')^2 - (Z'n)^2}{2(Z - Z')(nn')^2} &= \frac{\langle \Psi_{n',l,m}^{(Z')} (r, \theta, \phi) | \frac{1}{r} | \Psi_{n,l,m}^{(Z)} (r, \theta, \phi) \rangle}{\langle \Psi_{n',l,m}^{(Z')} (r, \theta, \phi) | \Psi_{n,l,m}^{(Z)} (r, \theta, \phi) \rangle}
 \end{aligned}$$

Next, we substitute in from Eq. (10), obtaining

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$$\begin{aligned}
\frac{(Zn')^2 - (Z'n)^2}{2(Z - Z')(nn')^2} &= \frac{\left\langle N_{n',l}^{(Z')} r^l L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) e^{-\left(\frac{Z}{n'}\right)r} Y_l^m(\theta, \phi) \left| \frac{1}{r} \right| N_{n,l}^{(Z)} r^l L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi) \right\rangle}{\left\langle N_{n',l}^{(Z')} r^l L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) e^{-\left(\frac{Z}{n'}\right)r} Y_l^m(\theta, \phi) \left| N_{n,l}^{(Z)} r^l L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi) \right\rangle} \\
&= \frac{\left\langle r^l L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) e^{-\left(\frac{Z}{n'}\right)r} Y_l^m(\theta, \phi) \left| \frac{1}{r} \right| r^l L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi) \right\rangle}{\left\langle r^l L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) e^{-\left(\frac{Z}{n'}\right)r} Y_l^m(\theta, \phi) \left| r^l L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi) \right\rangle} \\
&= \frac{\int_0^\infty \int_0^\pi \int_0^{2\pi} \left( r^l L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) e^{-\left(\frac{Z}{n'}\right)r} Y_l^m(\theta, \phi) \right)^* \left( \frac{1}{r} \right) \left( r^l L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi) \right) r^2 \sin \theta d\phi d\theta dr}{\int_0^\infty \int_0^\pi \int_0^{2\pi} \left( r^l L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) e^{-\left(\frac{Z}{n'}\right)r} Y_l^m(\theta, \phi) \right)^* \left( r^l L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Z}{n}\right)r} Y_l^m(\theta, \phi) \right) r^2 \sin \theta d\phi d\theta dr} \\
&= \frac{\int_0^\infty \left( r^l L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) e^{-\left(\frac{Z}{n'}\right)r} \right) \left( \frac{1}{r} \right) \left( r^l L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Z}{n}\right)r} \right) r^2 dr \left[ \int_0^\pi \int_0^{2\pi} (Y_l^m(\theta, \phi))^* Y_l^m(\theta, \phi) \sin \theta d\phi d\theta \right]}{\int_0^\infty \left( r^l L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) e^{-\left(\frac{Z}{n'}\right)r} \right) \left( \frac{1}{r} \right) \left( r^l L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Z}{n}\right)r} \right) r^2 dr \left[ \int_0^\pi \int_0^{2\pi} (Y_l^m(\theta, \phi))^* Y_l^m(\theta, \phi) \sin \theta d\phi d\theta \right]} \\
&= \frac{\int_0^\infty L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Z}{n'}\right)r} e^{-\left(\frac{Z}{n}\right)r} r^{2l+1} dr}{\int_0^\infty L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Z}{n'}\right)r} e^{-\left(\frac{Z}{n}\right)r} r^{2l+2} dr} \\
&= \frac{\int_0^\infty L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Zn'+Z'n}{nn'}\right)r} r^{2l+1} dr}{\int_0^\infty L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Zn'+Z'n}{nn'}\right)r} r^{2l+2} dr}
\end{aligned}$$

Thus, we have that

$$\frac{(Zn')^2 - (Z'n)^2}{2(Z - Z')(nn')^2} = \frac{\int_0^\infty L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Zn'+Z'n}{nn'}\right)r} r^{2l+1} dr}{\int_0^\infty L_{n'-(l+1)}^{2l+1} \left( \frac{2Zr}{n'} \right) L_{n-(l+1)}^{2l+1} \left( \frac{2Zr}{n} \right) e^{-\left(\frac{Zn'+Z'n}{nn'}\right)r} r^{2l+2} dr}.$$



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Suppose that we use the integrated Hellmann-Feynman theorem to approximate the change in ground state energy. We have the exact expression

$$E(\lambda_2) - E(\lambda_1) = \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \quad (11)$$

Next, suppose we do not know the exact ground state wave function,  $\Psi(\lambda_2)$ , for  $\hat{H}(\lambda_2)$ . However, we do know an approximate wave function,  $\Psi_{approx}(\lambda_2) \neq \Psi(\lambda_2)$ . Because of the variational principle, we know that any approximate wave function has too high an energy. That is, for any approximate wave function,

$$\frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) | \Psi(\lambda_2) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_2) \rangle} = E(\lambda_2) < \frac{\langle \Psi_{approx}(\lambda_2) | \hat{H}(\lambda_2) | \Psi_{approx}(\lambda_2) \rangle}{\langle \Psi_{approx}(\lambda_2) | \Psi_{approx}(\lambda_2) \rangle} \quad (12)$$

Equation (12) is true for *any* Hamiltonian.

**(d) Is it true that, for any approximate wave function for the ground state of any Hamiltonian,  $H(\lambda_2)$ ,**

$$E(\lambda_2) - E(\lambda_1) < \frac{\langle \Psi_{approx}(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi_{approx}(\lambda_2) | \Psi(\lambda_1) \rangle} ? \quad (13)$$

**Why or why not?**

This is ***not*** true. One way to see this is to write the approximate wave function as the exact wave function plus a small correction. Then we have that

$$\Psi_{approx}^\varepsilon(\lambda_2) = \Psi(\lambda_2) + \varepsilon \Delta \Psi$$

$\Psi_{approx}^\varepsilon$  is a legitimate approximate wave functions for any  $\varepsilon \neq 0$ ; since Eq. **(13)** must hold for *any* approximate wave function, it is clear that Eq. **(13)** must hold for every value of  $\varepsilon \neq 0$

Substitute into Eq. **(13)**. We have that

$$\begin{aligned} \frac{\langle \Psi_{approx}(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi_{approx}(\lambda_2) | \Psi(\lambda_1) \rangle} &= \frac{\langle \Psi(\lambda_2) + \varepsilon \Delta \Psi | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) + \varepsilon \Delta \Psi | \Psi(\lambda_1) \rangle} \\ &= \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle + \varepsilon \langle \Delta \Psi | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle + \varepsilon \langle \Delta \Psi | \Psi(\lambda_1) \rangle} \end{aligned}$$

Suppose that  $\varepsilon \Delta \Psi$  is small; that is, suppose that  $\Psi_{approx}(\lambda_2)$  is a good approximation to  $\Psi(\lambda_2)$ . Then, using the binomial theorem

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$$\begin{aligned}
& \frac{\langle \Psi_{approx}(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi_{approx}(\lambda_2) | \Psi(\lambda_1) \rangle} \\
&= \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle + \varepsilon \langle \Delta \Psi | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle \left( 1 + \varepsilon \frac{\langle \Delta \Psi | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \right)} \\
&= \frac{\langle \Psi(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle + \varepsilon \langle \Delta \Psi | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \left( 1 - \varepsilon \frac{\langle \Delta \Psi | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} + \varepsilon^2 \left( \frac{\langle \Delta \Psi | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \right)^2 - \dots \right) \\
&= \left( (E(\lambda_2) - E(\lambda_1)) + \varepsilon \frac{\langle \Delta \Psi | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \right) \left( 1 - \varepsilon \frac{\langle \Delta \Psi | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} + \varepsilon^2 \left( \frac{\langle \Delta \Psi | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \right)^2 - \dots \right)
\end{aligned}$$

If  $\varepsilon \Delta \Psi$  is very small, terms that have two factors of  $\varepsilon \Delta \Psi$  in them will be very small. (If this is not true for a given value of  $\varepsilon$ , reduce  $\varepsilon$  until it is true.) So we have that

$$\begin{aligned}
& \frac{\langle \Psi_{approx}(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi_{approx}(\lambda_2) | \Psi(\lambda_1) \rangle} \\
&= \left( (E(\lambda_2) - E(\lambda_1)) + \varepsilon \frac{\langle \Delta \Psi | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \right) \left( 1 - \varepsilon \frac{\langle \Delta \Psi | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} + \varepsilon^2 \left( \frac{\langle \Delta \Psi | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \right)^2 - \dots \right) \\
&\approx (E(\lambda_2) - E(\lambda_1)) - \varepsilon (E(\lambda_2) - E(\lambda_1)) \frac{\langle \Delta \Psi | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} + \varepsilon \frac{\langle \Delta \Psi | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \\
&\approx (E(\lambda_2) - E(\lambda_1)) + \varepsilon \frac{\langle \Delta \Psi | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle - (E(\lambda_2) - E(\lambda_1)) \langle \Delta \Psi | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle}
\end{aligned}$$

Eq. (13) and the previous equation require that

$$0 < \varepsilon \left( \frac{\langle \Delta \Psi | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle - (E(\lambda_2) - E(\lambda_1)) \langle \Delta \Psi | \Psi(\lambda_1) \rangle}{\langle \Psi(\lambda_2) | \Psi(\lambda_1) \rangle} \right)$$

$$0 < \varepsilon \left( \langle \Delta \Psi | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle - (E(\lambda_2) - E(\lambda_1)) \langle \Delta \Psi | \Psi(\lambda_1) \rangle \right)$$

for every value of  $\varepsilon \neq 0$ . However, if this equation hold for  $\varepsilon > 0$ , then it will not hold for  $\varepsilon < 0$ , and vice versa. It follows that there will always be some value of  $\varepsilon$  for which  $\Psi_{approx}^\varepsilon(\lambda_2) = \Psi(\lambda_2) + \varepsilon \Delta \Psi$  does not satisfy Eq. (13).

Another (faster, but not as nice mathematically) way to define a Hamiltonian operator with certain properties and then find a counterexample. Let

$$\hat{H}(\lambda_2) \Psi_0(\lambda_2) = -4 \Psi_0(\lambda_2)$$

$$\hat{H}(\lambda_2) \Psi_1(\lambda_2) = -3.9 \Psi_1(\lambda_2)$$

and then let

$$\langle \Psi_0(\lambda_2) | \Psi(\lambda_1) \rangle = .75$$

$$\langle \Psi_1(\lambda_2) | \Psi(\lambda_1) \rangle = .1$$

This is the *definition* of  $\hat{H}(\lambda_2)$ . For simplicity, choose  $E(\lambda_1) = 0$ . Using  $\Psi_{approx}(\lambda_2) = c_0 \Psi_0(\lambda_2) + c_1 \Psi_1(\lambda_2)$  we need only find values of  $c_0$  and  $c_1$  that violate our assumption. From Eq. (13),

$$-4 - 0 < \frac{\langle c_0 \Psi_0(\lambda_2) + c_1 \Psi_1(\lambda_2) | \hat{H}(\lambda_2) - \hat{H}(\lambda_1) | \Psi(\lambda_1) \rangle}{\langle c_0 \Psi_0(\lambda_2) + c_1 \Psi_1(\lambda_2) | \Psi(\lambda_1) \rangle}$$

$$-4 < \frac{c_0(-4)(.75) + c_1(-3.9)(.1)}{c_0(.75) + c_1(.1)}$$

$$-4 < \frac{-3c_0 - .39c_1}{(.75c_0 + .1c_1)}$$

If  $.75c_0 - .1c_1 > 0$ , then

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$$\begin{aligned}-4 &< \frac{-3c_0 - .39c_1}{(.75c_0 + .1c_1)} \\ -3c_0 - .4c_1 &< -3c_0 - .39c_1 \\ -.4c_1 &< -.39c_1 \\ 0 &< .01c_1 \\ 0 &< c_1\end{aligned}$$

So if  $.75c_0 - .1c_1 > 0$ , then  $c_1 < 0$  will violate the inequality in Eq. **(13)**. If  $.75c_0 - .1c_1 < 0$ , then (use the same argument)  $c_1 > 0$  will violate the inequality in Eq. **(13)**. Ergo, there is always a way to choose  $c_0$  and  $c_1$  so that Eq. **(13)** is not true.

### 3. Spin-Eigenfunctions and Slater Determinants.

$\begin{vmatrix} \psi_{4f_0} \alpha & \psi_{4f_1} \beta \end{vmatrix}$  is not an eigenfunction of the  $\hat{S}^2$  operator.

- a. Derive this result. That is, explicitly (using the a form for the  $\hat{S}^2$  operator) show that

$$\hat{S}^2 \begin{vmatrix} \psi_{4f_0} \alpha & \psi_{4f_1} \beta \end{vmatrix} \neq 0 \begin{vmatrix} \psi_{4f_0} \alpha & \psi_{4f_1} \beta \end{vmatrix} \quad (14)$$

( $S = 0$  is what we might expect for a state with  $M_s = 0$ .)

The easiest way to do this is to use the ladder operators. Specifically, we use the expression

$$\hat{S}_+ \hat{S}_- + \hat{S}_z^2 - \hbar \hat{S}_z = \hat{S}^2$$

and so, for two electrons, we have

$$\begin{aligned} \hat{S}^2 (1,2) &= (\hat{S}_+ (1) + \hat{S}_+ (2)) (\hat{S}_- (1) + \hat{S}_- (2)) \\ &\quad + (\hat{S}_z (1) + \hat{S}_z (2)) (\hat{S}_z (1) + \hat{S}_z (2)) \\ &\quad - \hbar \hat{S}_z (1) - \hbar \hat{S}_z (2) \\ &= \hat{S}_+ (1) \hat{S}_- (1) + \hat{S}_+ (1) \hat{S}_- (2) + \hat{S}_+ (2) \hat{S}_- (1) + \hat{S}_+ (2) \hat{S}_- (2) \\ &\quad + \hat{S}_z (1) \hat{S}_z (1) + \hat{S}_z (1) \hat{S}_z (2) + \hat{S}_z (2) \hat{S}_z (1) + \hat{S}_z (2) \hat{S}_z (2) \\ &\quad - \hbar \hat{S}_z (1) - \hbar \hat{S}_z (2) \end{aligned}$$

Next, we expand out the wave function. This gives

$$\begin{aligned} \begin{vmatrix} \psi_{4f_0} \alpha & \psi_{4f_1} \beta \end{vmatrix} &= \frac{1}{\sqrt{2}} (\psi_0(\mathbf{r}_1) \alpha(1) \psi_1(\mathbf{r}_2) \beta(2) - \psi_1(\mathbf{r}_1) \beta(1) \psi_0(\mathbf{r}_2) \alpha(2)) \\ &= \frac{1}{\sqrt{2}} (\psi_0(\mathbf{r}_1) \psi_1(\mathbf{r}_2) \alpha(1) \beta(2) - \psi_1(\mathbf{r}_1) \psi_0(\mathbf{r}_2) \beta(1) \alpha(2)). \end{aligned}$$

Now, we have that

$$\begin{aligned} \hat{S}_+ (1) \alpha(1) &= 0 \\ \hat{S}_+ (1) \beta(1) &= \hbar \sqrt{\frac{1}{2}(\frac{1}{2} + 1) - (-\frac{1}{2})(\frac{1}{2})} \alpha(1) \\ &= \hbar \alpha(1) \\ \hat{S}_- (1) \alpha(1) &= \hbar \sqrt{\frac{1}{2}(\frac{1}{2} + 1) - \frac{1}{2}(\frac{1}{2} - 1)} \beta(1) \\ &= \hbar \beta(1) \\ \hat{S}_+ (1) \beta(1) &= 0 \end{aligned}$$

And so

$$\begin{aligned}
\hat{S}^2(1,2)\alpha(1)\beta(2) &= \begin{bmatrix} \hat{S}_+(1)\hat{S}_-(1) + \hat{S}_+(1)\hat{S}_-(2) + \hat{S}_+(2)\hat{S}_-(1) + \hat{S}_+(2)\hat{S}_-(2) \\ \hat{S}_z(1)\hat{S}_z(1) + \hat{S}_z(1)\hat{S}_z(2) + \hat{S}_z(2)\hat{S}_z(1) + \hat{S}_z(2)\hat{S}_z(2) \\ -\hbar\hat{S}_z(1) - \hbar\hat{S}_z(2) \end{bmatrix} \alpha(1)\beta(2) \\
&= \hbar^2\alpha(1)\beta(2) + 0 + \hbar^2\beta(1)\alpha(2) + 0 \\
&\quad + \left(\hbar^2\left(\frac{1}{4}\right) + \hbar^2\left(\frac{1}{2}\right)\left(\frac{-1}{2}\right) + \hbar^2\left(\frac{1}{2}\right)\left(\frac{-1}{2}\right) + \hbar^2\left(\frac{-1}{2}\right)\left(\frac{-1}{2}\right)\right)\alpha(1)\beta(2) \\
&\quad - \hbar^2\left(\frac{1}{2} - \frac{1}{2}\right)\alpha(1)\beta(2) \\
&= \hbar^2(\alpha(1)\beta(2) + \beta(1)\alpha(2))
\end{aligned}$$

Similarly, we have that

$$\hat{S}^2(1,2)\beta(1)\alpha(2) = \hbar^2(\alpha(1)\beta(2) + \beta(1)\alpha(2))$$

Substituting in, we have that

$$\begin{aligned}
\hat{S}^2(1,2)\begin{vmatrix} \psi_{4f_0}\alpha & \psi_{4f_1}\beta \end{vmatrix} &= \frac{1}{\sqrt{2}}\left(\hat{S}^2(1,2)\psi_0(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\alpha(1)\beta(2) - \hat{S}^2(1,2)\psi_1(\mathbf{r}_1)\psi_0(\mathbf{r}_2)\beta(1)\alpha(2)\right). \\
&= \frac{1}{\sqrt{2}}\left(\psi_0(\mathbf{r}_1)\psi_1(\mathbf{r}_2)\hat{S}^2(1,2)\alpha(1)\beta(2) - \psi_1(\mathbf{r}_1)\psi_0(\mathbf{r}_2)\hat{S}^2(1,2)\beta(1)\alpha(2)\right). \\
&= \hbar^2\left[\frac{1}{\sqrt{2}}\begin{bmatrix} \psi_0(\mathbf{r}_1)\psi_1(\mathbf{r}_2)(\beta(1)\alpha(2) + \alpha(1)\beta(2)) \\ -\psi_1(\mathbf{r}_1)\psi_0(\mathbf{r}_2)(\beta(1)\alpha(2) + \alpha(1)\beta(2)) \end{bmatrix}\right]. \\
&= \hbar^2\begin{vmatrix} \psi_{4f_0}\beta & \psi_{4f_1}\alpha \end{vmatrix} + \hbar^2\begin{vmatrix} \psi_{4f_0}\alpha & \psi_{4f_1}\beta \end{vmatrix} \\
&\neq (\text{constant})\begin{vmatrix} \psi_{4f_0}\alpha & \psi_{4f_1}\beta \end{vmatrix}
\end{aligned}$$

b. Explain, in words, why  $\begin{vmatrix} \psi_{4f_0}\alpha & \psi_{4f_1}\beta \end{vmatrix}$  is not an eigenfunction of the  $\hat{S}^2$  operator.

It is not an eigenfunction because it “assigns” the electron in the  $4f^0$  orbital  $\alpha$  spin and the electron in the  $4f^1$  orbital  $\beta$  spin. Clearly it is also possible that the electron in the  $4f^0$  orbital could have  $\beta$  spin and the electron in the  $4f^1$  orbital could have  $\alpha$  spin. By “picking out” only one of the two spin-related possibilities, this Slater determinant fails to be an eigenfunction of  $\hat{S}^2$ . Said differently, since there is more than one way to use these orbitals to obtain a state with this value of  $M_s$ , the state isn’t an eigenfunction of  $\hat{S}^2$ . (That is, there are multiple Slater determinants with the same values for  $M_s$  (and also  $M_L$ , but this does not matter since we are not addressing eigenfunctions of  $\hat{L}^2$  in this problem).

## Part 2: Closed-Book Derivations and Problems. (20 points)

### 1. Asymptotic decay and shapes of $d$ -orbitals.

- a. We have seen that the wave functions for the Hydrogen atom be written as the product of a radial and an angular component,  $\Psi_{nl}(r) = R_{nl}(r)Y_l^m(\theta, \phi)$ . Below, plot the radial component of the 3d, 4d, and 5d orbitals for a one-electron atom. (That is, sketch (qualitatively)  $R_{3d}(r), R_{4d}(r), R_{5d}(r)$  vs.  $r$ .)

- b. For each of these orbitals, what is the behavior very close to the nucleus and very far from the nucleus. Use the following table to report your answers.

Radial Wave Function	Form Near the Nucleus	Form Far from the nucleus
$R_{3d}(r)$	$\sim r^2$ (near the nucleus the wave function looks like $r^l$ )	$\sim r^2 e^{-\frac{Z}{3}r}$ The wave function looks like $r^l e^{-\frac{Z}{n}r} L_{n-l-1}^{2l+1}\left(\frac{2Zr}{n}\right)$ $= r^l e^{-\frac{Z}{n}r} (a_0 + a_1 r + \dots a_{n-l-1} r^{n-l-1})$ $\sim r^{n-l-1} r^l e^{-\frac{Z}{n}r}$ $\sim r^{n-1} e^{-\frac{Z}{n}r}$
$R_{4d}(r)$	$\sim r^2$	$\sim r^3 e^{-\left(\frac{Z}{4}\right)r}$
$R_{5d}(r)$	$\sim r^2$	$\sim r^4 e^{-\left(\frac{Z}{5}\right)r}$

(Neglect terms that are smaller than the “leading order” terms included in the forms reported here. In this format, constant factors (e.g., normalization) are not important.)

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**2. Show that  $[\hat{S}^2, \hat{S}_z] = 0$ . You may need to know that  $[\hat{S}_x, \hat{S}_y] = i\hbar\hat{S}_z$ ,**

$$[\hat{S}_y, \hat{S}_z] = i\hbar\hat{S}_x, \text{ and } [\hat{S}_z, \hat{S}_x] = i\hbar\hat{S}_y$$

$$[\hat{S}^2, \hat{S}_z] = [\hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2, \hat{S}_z]$$

$$= [\hat{S}_x^2, \hat{S}_z] + [\hat{S}_y^2, \hat{S}_z] + \cancel{[\hat{S}_z^2, \hat{S}_z]}$$

$$= \hat{S}_x [\hat{S}_x, \hat{S}_z] + [\hat{S}_x, \hat{S}_z] \hat{S}_x + \hat{S}_y [\hat{S}_y, \hat{S}_z] + [\hat{S}_y, \hat{S}_z] \hat{S}_y$$

$$= \hat{S}_x (-i\hbar\hat{S}_y) + (-i\hbar\hat{S}_y) \hat{S}_x + \hat{S}_y (i\hbar\hat{S}_x) + (i\hbar\hat{S}_x) \hat{S}_y$$

$$= i\hbar (-\hat{S}_x\hat{S}_y - \hat{S}_y\hat{S}_x) + i\hbar (\hat{S}_y\hat{S}_x + \hat{S}_x\hat{S}_y)$$

$$= 0$$



### 3. Integral of Laguerre functions (n,n+1):

In the homework, we derived the expression:

$$\int_0^{\infty} x^{p+1} e^{-x} \sum_{m=0}^{\infty} \sum_{n=0}^{\infty} L_m^p(x) L_n^p(x) s^m t^n dx = (1-s-t+st) \sum_{k=0}^{\infty} \frac{(p+1+k)!}{k!} s^k t^k$$

By grouping terms with equal powers of  $s$  and  $t$ , derive an expression for the following integral (for  $m \geq 0$ ).

$$\int_0^{\infty} x^{p+1} e^{-x} L_m^p(x) L_{m+1}^p(x) dx =$$

Pulling the factor of  $(1-s-t+st)$  into the summation, we have that

$$(1-s-t+st) \sum_{k=0}^{\infty} \frac{(p+1+k)!}{k!} s^k t^k = \sum_{k=0}^{\infty} \frac{(p+1+k)!}{k!} (s^k t^k - s^{k+1} t^k - s^k t^{k+1} + s^{k+1} t^{k+1})$$

We can write this as

$$\begin{aligned} (1-s-t+st) \sum_{k=0}^{\infty} \frac{(p+1+k)!}{k!} s^k t^k &= \sum_{k=0}^{\infty} a_k s^k t^k + \sum_{k=0}^{\infty} b_k s^{k+1} t^k + \sum_{k=0}^{\infty} c_k s^k t^{k+1} + \sum_{k=0}^{\infty} d_k s^{k+1} t^{k+1} \\ &= a_0 + \sum_{k=1}^{\infty} (a_k + d_{k-1}) s^k t^k + \sum_{k=0}^{\infty} b_k s^{k+1} t^k + \sum_{k=0}^{\infty} c_k s^k t^{k+1} \end{aligned}$$

where the coefficients  $a_k, b_k, c_k, d_k$  are easily determined to be

$$a_k = d_k = \frac{(p+1+k)!}{k!} = -b_k = -c_k.$$

The integral we desire,

$$\int_0^{\infty} x^{p+1} e^{-x} L_k^p(x) L_{k+1}^p(x) dx$$

is the coefficient of  $s^k t^{k+1}$ . It must be equal to  $b_k$ , then, since the coefficients of each power of  $s^k t^l$  must be equal. We have, then, that

$$\int_0^{\infty} x^{p+1} e^{-x} L_k^p(x) L_{k+1}^p(x) dx = b_k = -\frac{(p+1+k)!}{k!}. \quad (15)$$

#### 4. Term Symbols and such for Cerium.

- a. Cerium has a [closed subshell]  $4f^1 5d^1$  configuration. What are the term symbols?

We have one electron with  $l = 3$  and one with  $l = 2$ . The possible values of  $L$  are then  $|l_2 - l_1| = 1 \leq L \leq 5 = |l_2 + l_1|$ . Similarly, the spins can be paired (triplet,  $S = 1$ ) or opposed (singlet,  $S = 0$ ). This gives, as terms,

$$^3P, ^3D, ^3F, ^3G, ^3H, ^1P, ^1D, ^1F, ^1G, ^1H$$

- b. What is the predicted order of states according to Hund's Rules?

$$^3H, ^3G, ^3F, ^3D, ^3P, ^1H, ^1G, ^1F, ^1D, ^1P$$

- c. What is the predicted order of states (one cannot do this completely, but order states as best you can) using the Russell-Meggers and Kutzelnigg-Morgan rules?

Odd parity singlet states are lowest.  $(-1)^{L+l_1+l_2} = (-1)^{L+5} = -1$  for  $L = 2, 4$ .

The optimal value of  $L$  is  $L_{opt} \approx \frac{2+3}{\sqrt{2}} \approx 3.53$ , which is closer to 4 than 2.

(1) So  $E[^1G] < E[^1D]$ .

Among triplet states, odd parity is favorable, but this competes with the optimum  $L$  rule. Clearly the "best" triplet state is the odd-parity, near-optimal  $^3G$ . We can state that this state will be lower than energy than the other odd-parity triplet state in accord with the maximum  $L$  rule.

(2) This gives,  $E[^3G] < E[^3D]$ .

Among the even parity-triplet states, we have only the optimum  $L$  rule. The same is true for the even parity singlet states. This gives

$$(3) \quad E[^3F] < E[^3H] < E[^3P]$$

$$(4) \quad E[^1F] < E[^1H] < E[^1P]$$

Since the  $^3P$  has a far from optimal  $L$  and the  $^3H$  has an  $L$  scarcely more optimal than the more favorable odd-parity  $^3D$ , we surmise,

$$(5) \quad E[^3G] < E[^3D] \lesssim E[^3H] < E[^3P]$$

The only question is whether  $E[^3F] < E[^3D]$  or  $E[^3F] > E[^3D]$  or, mathematically, that  $E[^3F] \leq E[^3D]$ . This leaves two possible approximate orders, which we can express in the following equation.

$$E[^1G] < E[^1D] < E[^3G] < [E[^3F] \leq E[^3D]] \lesssim E[^3H] < E[^3P] < E[^1F] < E[^1H] < E[^1P]$$

## Part 3: Multiple-Choice; Short-Answer (35 points)

*The following terms enter into the Schrödinger equation for a 2-electron diatomic molecule. Use the following notation in problems 1 and 2.*

$$\begin{aligned}\hat{V}_{nn} &\equiv \frac{Z_1 Z_2}{|\mathbf{R}_1 - \mathbf{R}_2|} & \hat{T}_n &\equiv -\frac{\nabla_{\mathbf{R}_1}^2}{2M_1} - \frac{\nabla_{\mathbf{R}_2}^2}{2M_2} \\ \hat{V}_{ee} &\equiv \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} & \hat{T}_e &\equiv -\frac{\nabla_{\mathbf{r}_1}^2}{2} - \frac{\nabla_{\mathbf{r}_2}^2}{2} \\ \hat{V}_{ne} &\equiv -\frac{Z_1}{|\mathbf{r}_1 - \mathbf{R}_1|} - \frac{Z_2}{|\mathbf{r}_1 - \mathbf{R}_2|} - \frac{Z_1}{|\mathbf{r}_2 - \mathbf{R}_1|} - \frac{Z_2}{|\mathbf{r}_2 - \mathbf{R}_2|}\end{aligned}$$

1. Using the preceding notation, write the Schrödinger equation for the electrons in the Born-Oppenheimer Approximation.

$$\left(\hat{T}_e + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn}\right)\psi_e(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_1, \mathbf{R}_2) = U_{BO}(\mathbf{R}_1, \mathbf{R}_2)\psi_e(\mathbf{r}_1, \mathbf{r}_2, \mathbf{R}_1, \mathbf{R}_2)$$

2. Using the preceding notation and your result from problems 1, write the Schrödinger equation for the nuclei in the Born-Oppenheimer Approximation.

$$\left(\hat{T}_n + U_{BO}(\mathbf{R}_1, \mathbf{R}_2)\right)\chi_n(\mathbf{R}_1, \mathbf{R}_2) = E_{BO}\chi_n(\mathbf{R}_1, \mathbf{R}_2)$$

3. One Bohr is about

- (a) 27 eV (c)  $10^{12}$  Hz  
(b) .5 Angstroms (d) .1 nm (nanometer)

4. One wave number ( $1 \text{ cm}^{-1}$ ) is about

- (a) 10 kcal/mol (c)  $10^{-8}$  Bohr  
(b)  $5 \cdot 10^{-6}$  Hartree (d) .01 eV

5. For which of the following systems is the Born-Oppenheimer approximation most justified? In other words, neglecting all other effects, for which system do you expect corrections to the Born-Oppenheimer approximation will be least important.

- (a)  $C_{60}$  (c)  $UF_6$   
(b)  $H_2$  (d)  $Si_{60}$

6. Write the electronic Schrödinger Equation for the Lithium atom in SI units, showing the dependence on  $\hbar$ ,  $e$ ,  $\epsilon_0$ , and  $m_e$ . You may use the Born-Oppenheimer approximation.

$$\left[ \sum_{i=1}^3 \left( -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{3e^2}{4\pi\epsilon_0 r_i} \right) + \sum_{i=1}^2 \sum_{j=i+1}^3 \frac{e^2}{4\pi\epsilon_0 |\mathbf{r}_i - \mathbf{r}_j|} \right] \Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \mathbf{r}_3, \sigma_3) = E \Psi(\mathbf{r}_1, \sigma_1; \mathbf{r}_2, \sigma_2; \mathbf{r}_3, \sigma_3)$$

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*Using separation of variables, the wave function for the hydrogen atom can be written as*

$$\Psi_{n,l,m}(\mathbf{r}) = R_{n,l}(r) Y_l^m(\theta, \phi).$$

7. Write the Schrodinger equation for radial wave function,  $R_{n,l}(r)$ , in the hydrogen atom. You may use atomic units.

$$\left( -\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{l(l+1)}{2r^2} - \frac{1}{r} \right) R_{n,l}(r) = E_n R_{n,l}(r)$$

- 8,9. Write the energy formula for the ground and excited states of a one-electron atom with atomic number  $Z$ .

$$\text{-----} \frac{-Z^2}{2n^2} \text{-----} \quad \text{In atomic units}$$

$$\text{-----} -\frac{Z^2 e^4 m_e}{2n^2 (4\pi\epsilon_0)^2 \hbar^2} \text{-----} \quad \text{In terms of } \hbar, m_e, e, \epsilon_0.$$

- 10-12. For each of the following orbitals, values of  $n$ ,  $l$ , and  $m$  (when appropriate). Here  $n$  is the principle quantum number,  $l$  is the angular momentum quantum number, and  $m$  is the magnetic quantum number.

orbital	$n$	$l$	$m$
$2p_x$	2	1	(not an eigenvalue)
$4s$	4	0	0
$6d_{2z^2-x^2-y^2}$	6	2	0

13.  $Y_l^m(\theta, \phi)$  is called a(n)

- |                                    |                               |
|------------------------------------|-------------------------------|
| (a) associated Legendre polynomial | (e) Legendre polynomial       |
| (b) associated Laguerre polynomial | (f) Laguerre polynomial       |
| (c) associated Lagrange polynomial | (g) Lagrange polynomial       |
| (d) Linus-Pauling polynomial       | <b>(h) spherical harmonic</b> |

14. Which of the following statements are true of electronic systems:

- (a) Wave functions must be antisymmetric with respect to exchange of electronic positions.  
**(b) Wave functions must respect the equivalence of electrons.**  
(c) The Hamiltonian must be symmetric with respect to exchange of electronic positions.  
**(d) Wave functions must be antisymmetric with respect to when two electrons' coordinates (both space and spin) are exchanged.**  
(e) No two electrons can ever be in the same state.

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15. In terms of the Bohr magneton,  $\beta_e$ , the magnetic moment of an electron with spin-quantum number  $m_s$  is

(a)  $\mu_s \approx -m_s \frac{\beta_e}{\hbar}$

(c)  $\mu_s \approx +m_s \frac{\beta_e}{\hbar}$

(b)  $\mu_s \approx -\frac{1}{2} m_s \frac{\beta_e}{\hbar}$

(d)  $\mu_s \approx -2m_s \frac{\beta_e}{\hbar}$

16. Let  $\Psi(r_1, \sigma_1; r_2, \sigma_2; \dots; r_N, \sigma_N)$  be antisymmetric with respect to exchange of any two electronic coordinates. Show that the probability of two electrons with the same spin being at the same location is zero.

$$\Psi(r_1, \sigma_1; r_2, \sigma_2; \dots; r_N, \sigma_N) = -\Psi(r_2, \sigma_2; r_1, \sigma_1; \dots; r_N, \sigma_N)$$

If  $r_1 = r_2$  and  $\sigma_1 = \sigma_2$ , then

$$\Psi(r_1, \sigma_1; r_1, \sigma_1; \dots; r_N, \sigma_N) = -\Psi(r_1, \sigma_1; r_1, \sigma_1; \dots; r_N, \sigma_N)$$

$$2\Psi(r_1, \sigma_1; r_1, \sigma_1; \dots; r_N, \sigma_N) = 0$$

$$\Psi(r_1, \sigma_1; r_1, \sigma_1; \dots; r_N, \sigma_N) = 0$$

Then

$$|\Psi(r_1, \sigma_1; r_1, \sigma_1; \dots; r_N, \sigma_N)|^2 = 0$$

17. Write a Slater determinant wave function for the  $1s^2 2s^1$  state of the Lithium atom. Do not use the “shorthand” notation. Denote the spatial part of the 1s orbital with  $\psi_{1s}(r)$  and the spatial part of the 2s orbital with  $\psi_{2s}(r)$ .

$$\Psi_{Li}(r_1, \sigma_1, r_2, \sigma_2, r_3, \sigma_3) = \frac{1}{\sqrt{6}} \begin{vmatrix} \psi_{1s}(r_1)\alpha(1) & \psi_{1s}(r_1)\beta(1) & \psi_{2s}(r_1)\alpha(1) \\ \psi_{1s}(r_2)\alpha(2) & \psi_{1s}(r_2)\beta(2) & \psi_{2s}(r_2)\alpha(2) \\ \psi_{1s}(r_3)\alpha(3) & \psi_{1s}(r_3)\beta(3) & \psi_{2s}(r_3)\alpha(3) \end{vmatrix}$$

In the next few problems, we will consider Slater determinants for the Boron atom with electron configuration  $1s^2 2s^2 2p^1$  and  $M_S = \frac{1}{2}$  and  $M_L = 0$ .

18. Write a Slater determinant appropriate for a *restricted* Hartree-Fock (RHF) approximation. (You can use the shorthand notation.)

$$\begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{2s}\beta & \psi_{2p_0}\alpha \end{vmatrix} = \begin{vmatrix} \psi_{1s}\alpha & \psi_{1s}\beta & \psi_{2s}\alpha & \psi_{2s}\beta & \psi_{2p_z}\alpha \end{vmatrix}$$

19. Write a Slater determinant appropriate for an *unrestricted* Hartree-Fock (UHF) approximation. (You can use the shorthand notation.)

$$\begin{vmatrix} \psi_{1s}\alpha & \psi'_{1s}\beta & \psi_{2s}\alpha & \psi'_{2s}\beta & \psi_{2p_0}\alpha \end{vmatrix} = \begin{vmatrix} \psi_{1s}\alpha & \psi'_{1s}\beta & \psi_{2s}\alpha & \psi'_{2s}\beta & \psi_{2p_z}\alpha \end{vmatrix}$$

**20,21. Is the RHF wave function from part 18 an eigenfunction of**

$\hat{S}^2$	Yes	No
$\hat{L}^2$	Yes	No

**22,23. Is the UHF wave function from part 19 an eigenfunction of**

$\hat{S}^2$	Yes	No
$\hat{L}^2$	Yes	No

Suppose we perform the Hartree-Fock procedure, and find the orbitals in the Slater determinants from problems 18 and 19 that minimize the energy. The result obtained using the wave function from problem 18 is the restricted-Hartree Fock energy ( $E_{RHF}$ ) and the result obtained using the wave function from problem 19 is the unrestricted Hartree-Fock energy ( $E_{UHF}$ ).

**24. True or False. The unrestricted Hartree Fock energy is strictly less than the restricted Hartree-Fock energy. ( $E_{UHF} < E_{RHF}$ )**

(a) True

(b) False

Suppose we perform both restricted (RHF) and unrestricted (UHF) Hartree-Fock calculations for the Beryllium atom in its ground state ( $1s^2 2s^2$ ) configuration.

**25. True or False. The restricted Hartree Fock energy for Beryllium is strictly less than the unrestricted Hartree-Fock energy. ( $E_{UHF} < E_{RHF}$ )**

(a) True

(b) False (they are equal in this case)

**26. Consider two states of the Lithium atom, the ground state ( $1s^2 2s^1$ ) and the highly excited  $1s^2 4f^1$  configuration. We perform both restricted and unrestricted Hartree-Fock calculations on both states. The 1s orbitals in the RHF and UHF calculations are compared in each case. Which of the following do you expect to be true.**

(a) The 1s orbitals computed from the UHF and RHF calculations are more similar for the  $1s^2 2s^1$  state.

(b) The 1s orbitals computed from the UHF and RHF calculations are more similar for the  $1s^2 4f^1$  state.

The ground state term for Promethium ( $[\text{closed shell}] 4f^5 6s^2$  configuration) is  ${}^6H$ .

**27. What are the possible values of the total angular momentum quantum number,  $J$ , in Promethium?**

$L = 5$ , and  $2S + 1 = 6 \rightarrow S = \frac{5}{2}$ .

$$|L - S| = |5 - \frac{5}{2}| = \frac{5}{2} \leq J \leq \frac{15}{2} = |5 + \frac{5}{2}| = |L + S|$$

So  $J = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}, \frac{11}{2}, \frac{13}{2}, \frac{15}{2}$ .

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28. For the ground state term in Promethium, list all the possible eigenvalues of  $M_J$ .

Promethium is a less than half-filled shell, so the smallest  $J$  is the best. Thus, we have that

$$\begin{aligned} M_J &= -J, -J+1, \dots, J \\ &= -\frac{5}{2}, -\frac{3}{2}, -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}. \end{aligned}$$

29. Sketch the effective nuclear charge as a function of distance for the Magnesium dication ( $Mg^{2+}$ ). (The atomic number of Magnesium is 12). Carefully label the value of the effective nuclear charge at the nucleus and infinitely far from the nucleus.

30. True or False. For each electron in a many-electron atom, we can determine its angular momentum about the  $z$  axis,  $\hbar m_l$ .

(a) true

(b) false

31. Which of the following operators commute with  $\hat{L}_x$ . (There may be more than one answer.)

(a)  $\hat{J}^2$

(d)  $\hat{L}_x$

(g)  $\hat{S}_x$

(j)  $\hat{J}_x$

(b)  $\hat{S}^2$

(e)  $\hat{L}_y$

(h)  $\hat{S}_y$

(k)  $\hat{J}_y$

(c)  $\hat{L}^2$

(f)  $\hat{L}_z$

(i)  $\hat{S}_z$

(l)  $\hat{J}_z$

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32. What are the term symbols for the  $p^3$  configuration? Clearly mark the ground state term.

	$M_L$		
$M_S$	2	1	0
$\frac{3}{2}$			$ \psi_1\alpha \ \psi_0\alpha \ \psi_{-1}\alpha $
$\frac{1}{2}$	$ \psi_1\alpha \ \psi_1\beta \ \psi_0\alpha $	$ \psi_1\alpha \ \psi_0\alpha \ \psi_0\beta $ $ \psi_1\alpha \ \psi_0\alpha \ \psi_0\beta $	$ \psi_1\beta \ \psi_0\alpha \ \psi_{-1}\alpha $ $ \psi_1\alpha \ \psi_0\beta \ \psi_{-1}\alpha $ $ \psi_1\alpha \ \psi_0\alpha \ \psi_{-1}\beta $

Here the notation is that  $\psi_{2p_{m_l}}(\mathbf{r}) = \psi_{m_l}(\mathbf{r})$ . Using the “color-coding” trick, we cross out terms to obtain,  $^4S$ ,  $^2D$ , and  $^2P$ . The  $^4S$  is the ground state term.

33,34. For each of the following operators, if the Slater determinant  $|\psi_{2p_1}\alpha \ \psi_{2p_0}\alpha \ \psi_{2p_{-1}}\alpha|$  is an eigenfunction of the operator, fill in its eigenvalue. Otherwise, write in “not an eigenvalue.”

$$\begin{aligned}
 \hat{L}^2 |\psi_{2p_1}\alpha \ \psi_{2p_0}\alpha \ \psi_{2p_{-1}}\alpha| &= \left[ \begin{array}{c} 0 \end{array} \right] |\psi_{2p_1}\alpha \ \psi_{2p_0}\alpha \ \psi_{2p_{-1}}\alpha| \\
 \hat{S}^2 |\psi_{2p_1}\alpha \ \psi_{2p_0}\alpha \ \psi_{2p_{-1}}\alpha| &= \left[ \begin{array}{c} \hbar^2 \left(\frac{3}{2}\right)\left(\frac{5}{2}\right) \end{array} \right] |\psi_{2p_1}\alpha \ \psi_{2p_0}\alpha \ \psi_{2p_{-1}}\alpha| \\
 &= \frac{15}{4} \hbar^2 |\psi_{2p_1}\alpha \ \psi_{2p_0}\alpha \ \psi_{2p_{-1}}\alpha| \\
 \hat{L}_z |\psi_{2p_1}\alpha \ \psi_{2p_0}\alpha \ \psi_{2p_{-1}}\alpha| &= \left[ \begin{array}{c} 0 \end{array} \right] |\psi_{2p_1}\alpha \ \psi_{2p_0}\alpha \ \psi_{2p_{-1}}\alpha| \\
 \hat{J}_z |\psi_{2p_1}\alpha \ \psi_{2p_0}\alpha \ \psi_{2p_{-1}}\alpha| &= \left[ \begin{array}{c} 0 + \hbar \frac{3}{2} \end{array} \right] |\psi_{2p_1}\alpha \ \psi_{2p_0}\alpha \ \psi_{2p_{-1}}\alpha| \\
 &= \frac{3}{2} \hbar |\psi_{2p_1}\alpha \ \psi_{2p_0}\alpha \ \psi_{2p_{-1}}\alpha|
 \end{aligned} \tag{16}$$

We wish to approximate the ground state wave function of the Helium atom with a Slater determinant,

$$\Psi_\zeta \equiv \frac{1}{\sqrt{2}} |\psi_1\alpha \ \psi_1\beta| \tag{17}$$

where

$$\psi_1(\mathbf{r}) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r}; \zeta > 0. \tag{18}$$

We have that

$$\begin{aligned}
 E(\zeta) &\equiv \frac{\left\langle \Psi_1 \left| \left( -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \right| \Psi_1 \right\rangle}{\langle \Psi_1 | \Psi_1 \rangle} \\
 &= -\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - 2)
 \end{aligned} \tag{19}$$



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**35. Using the Slater determinant in Eq. (17), what energy do you obtain if you perform the Hartree-Fock method with the orbitals given in Eq. (18).**

The Hartree-Fock method finds the lowest-energy Slater determinant of a given form. Since Eq. (19) is the energy expression, we need to find the value of  $\zeta$  for which the energy is minimized. At the minimum,  $\frac{\partial E}{\partial \zeta} = 0$ . Thus

$$\begin{aligned} 0 &= \frac{\partial}{\partial \zeta} \left( -\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - 2) \right) \\ &= -2\zeta + \frac{5}{8} + 4\zeta - 4 \\ &= 2\zeta - \frac{27}{8} \\ \zeta &= \frac{27}{16} = 1.6875 \end{aligned} \tag{20}$$

We substitute back into Eq. (19), and obtain

$$\begin{aligned} E_{HF} &\rightarrow -\left(\frac{27}{16}\right)^2 + \frac{5}{8}\left(\frac{27}{16}\right) + 2\left(\frac{27}{16}\right)\left(\frac{27}{16} - 2\right) \\ &= \left(\frac{27}{16}\right)\left(-\frac{27}{16} + \frac{5}{8} - 2\left(\frac{5}{16}\right)\right) \\ &= \left(-\frac{27}{16}\right)^2 \\ &= -2.848 \text{ Hartree} \end{aligned} \tag{21}$$