

Test 1

Chemistry 3BB3; Winter 2003

Part 1. Multiple-Choice/Short Answer (3 points each) (65 points)

1. The Schrödinger equation for a 2-electron, 2-atom molecule is written below, in atomic units. Cross out the terms that are ignored in the Born-Oppenheimer approximation.

$$\begin{aligned}
 & \cancel{\chi_n(\mathbf{R}_1, \mathbf{R}_2) \left(-\frac{\nabla_{\mathbf{R}_1}^2}{2M_1} - \frac{\nabla_{\mathbf{R}_2}^2}{2M_2} \right) \psi_e(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2)} - \cancel{\frac{\nabla_{\mathbf{R}_1} \chi_n(\mathbf{R}_1, \mathbf{R}_2) \cdot \nabla_{\mathbf{R}_1} \psi_e(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2)}{M_1}} \\
 & - \cancel{\frac{\nabla_{\mathbf{R}_2} \chi_n(\mathbf{R}_1, \mathbf{R}_2) \cdot \nabla_{\mathbf{R}_2} \psi_e(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2)}{M_2}} + \psi_e(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2) \left(-\frac{\nabla_{\mathbf{R}_1}^2}{2M_1} - \frac{\nabla_{\mathbf{R}_2}^2}{2M_2} \right) \chi_n(\mathbf{R}_1, \mathbf{R}_2) \\
 & + \chi_n(\mathbf{R}_1, \mathbf{R}_2) \left(-\frac{\nabla_{\mathbf{r}_1}^2}{2} - \frac{\nabla_{\mathbf{r}_2}^2}{2} + \frac{Z_1 Z_2}{|\mathbf{R}_1 - \mathbf{R}_2|} - \frac{Z_1}{|\mathbf{r}_1 - \mathbf{R}_1|} - \frac{Z_2}{|\mathbf{r}_1 - \mathbf{R}_2|} - \frac{Z_1}{|\mathbf{r}_2 - \mathbf{R}_1|} - \frac{Z_2}{|\mathbf{r}_2 - \mathbf{R}_2|} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \psi_e(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2) \\
 & = E \chi_n(\mathbf{R}_1, \mathbf{R}_2) \psi_e(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2)
 \end{aligned}$$

2. Using the following definitions,

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

the Schrödinger equation for the electrons, in the Born-Oppenheimer approximation, can be written as

$$(\hat{T}_e + V_{ne} + V_{ee} + V_{nn})\Psi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2) = U(\mathbf{R}_1, \mathbf{R}_2)\Psi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}_1, \mathbf{R}_2)$$

What is the Schrödinger equation for the nuclei in the Born-Oppenheimer approximation?

$$(\hat{T}_n + U(\mathbf{R}_1, \mathbf{R}_2))\chi_n(\mathbf{R}_1, \mathbf{R}_2) = E^{BO}\chi_n(\mathbf{R}_1, \mathbf{R}_2)$$

3. Number the following units in order of *increasing* energy

___5___ 1 Hartree ___1___ 1 Hertz ___3___ 1 kJ/mol
 ___4___ 1 electron volt ___2___ 1 cm⁻¹

4. The atomic unit of length is the

- (a) Bohr.
- (b) Schrödinger.
- (c) Slater.
- (d) Oppenheimer.
- (e) None of the above.

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5. Write the Schrödinger equation for the Hydrogen atom and do not use atomic units. That is, include the explicit dependence on \hbar , m_e , e , ε_0 , etc. explicit.

$$\left(-\frac{\hbar^2}{2m_e}\nabla^2 - \frac{Ze^2}{4\pi\varepsilon_0 r}\right)\Psi(r,\theta,\phi) = E\Psi(r,\theta,\phi)$$

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

$$\text{_____} E_n = \frac{-Z^2}{2n^2} \text{_____}$$

a. In atomic units

$$\text{_____} E_n = -\left(\frac{Z^2}{2n^2}\right)\left(\frac{e^4 m_e}{(4\pi\varepsilon_0)^2 \hbar^2}\right) \cdot \text{_____}$$

b. in terms of \hbar , m_e , e , ε_0

7. For the state with principle quantum number, n , the orbital angular momentum quantum number, l , is restricted to the values

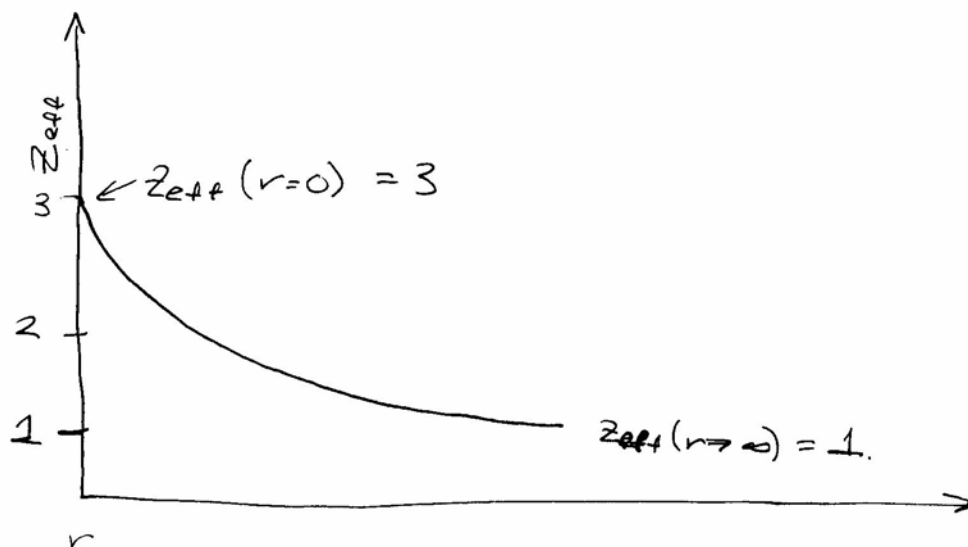
- (a) $l = 0, 1, 2, \dots, n$
- (b) $l = 1, 2, \dots, n$
- (c) $l = 0, 1, 2, \dots, n - 1$**
- (d) $l = 1, 2, \dots, n - 1$
- (e) $-n, -n + 1, \dots, n - 1, n$
- (f) $-n + 1, -n + 2, \dots, n - 2, n - 1$
- (g) none of the above

8. The radial eigenfunctions of the Hydrogen atom are most simply expressed in terms of

- (a) The associated Legendre polynomials
- (b) The Schrödinger polynomials
- (c) The Slater-type orbitals
- (d) The generalized Jacobi functions
- (e) The associated Laguerre polynomials**
- (f) The Linus Pauling orbitals
- (g) none of the above

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9. Sketch the dependence of the effective nuclear charge of the Lithium atom versus the distance from the nucleus. Make sure you label the values of the effective nuclear charge at $r = 0$ and as $r \rightarrow \infty$.



10. Write a Slater determinantal wave function that approximates the ground state of the Boron atom. Assume the 2p electron is in the $2p_z$ orbital.

$$\Phi_B \equiv \frac{1}{\sqrt{5!}} \begin{vmatrix} \psi_{1s}(r_1)\alpha(1) & \psi_{1s}(r_1)\beta(1) & \psi_{2s}(r_1)\alpha(1) & \psi_{2s}(r_1)\beta(1) & \psi_{2p_z}(r_1)\alpha(1) \\ \psi_{1s}(r_2)\alpha(2) & \psi_{1s}(r_2)\beta(2) & \psi_{2s}(r_2)\alpha(2) & \psi_{2s}(r_2)\beta(2) & \psi_{2p_z}(r_2)\alpha(2) \\ \psi_{1s}(r_3)\alpha(3) & \psi_{1s}(r_3)\beta(3) & \psi_{2s}(r_3)\alpha(3) & \psi_{2s}(r_3)\beta(3) & \psi_{2p_z}(r_3)\alpha(3) \\ \psi_{1s}(r_4)\alpha(4) & \psi_{1s}(r_4)\beta(4) & \psi_{2s}(r_4)\alpha(4) & \psi_{2s}(r_4)\beta(4) & \psi_{2p_z}(r_4)\alpha(4) \\ \psi_{1s}(r_5)\alpha(5) & \psi_{1s}(r_5)\beta(5) & \psi_{2s}(r_5)\alpha(5) & \psi_{2s}(r_5)\beta(5) & \psi_{2p_z}(r_5)\alpha(5) \end{vmatrix}$$

11. Why do the 2p orbitals fill after the 2s orbitals. That is, why is the electron configuration of Be $1s^2 2s^2$ instead of $1s^2 2p^2$ or $1s^2 2s^1 2p^1$? (The answer should be in words, but it can be very brief. WRITE NEATLY!!)

The 2p orbitals have less density near the nucleus than the 2s-orbital, and so they are “shielded” from the nuclear charge by the 1s-electrons. For this reason, the “effective nuclear charge” felt by the 2p electrons is less than that of the 2s electrons, and since the energy of an orbital is approximately

$$E_i \equiv -\frac{Z_{\text{eff}}^2}{2n^2} \quad (1)$$

the 2p-orbitals have higher energy than the 2s-electrons.

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12. What is the wave function for an electron in a one-electron atom with atomic number Z , principle quantum number n , magnetic quantum number m , and the maximum value of the angular momentum quantum number, L ? You may ignore the normalization constant.

$$\Psi(r, \theta, \phi) \propto r^l e^{-Zr/l+1} Y_l^m(\theta, \phi)$$

13. 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 eigenfunction of \hat{L}_z ; none)
$4s$	4	0	0
$6f_{(2z^2-3x^2-3y^2)}$	6	3	0

Cerium has an electron configuration of $[\text{Xe}]6s^2 4f^1 5d^1$.

15. List the term symbols associated with Cerium's ground state in order of increasing energy (ground state first).

We need only consider the $4f^1$ and $5d^1$ electrons. The $4f^1$ term is 2F and the $5d^1$ term is 2D . If the orbital angular momenta are aligned, then $L_{\max} = 3 + 2 \rightarrow H$ -type term. If the orbital angular momenta are opposed, then $L_{\min} = |3 - 2| \rightarrow P$ -type term. So there are H, G, F, D , and P -type terms

If the spin-angular momenta are aligned, then $S_{\max} = \frac{1}{2} + \frac{1}{2} \rightarrow$ triplet state. If the spin-angular momenta are opposed, then $S_{\min} = |1 - 1| = 0 \rightarrow$ singlet state. So we have that the terms are

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

This is in order of increasing energy, since "big L" and "big S" are good.

16. For the ground state term of Cerium, what values of J are allowed. Which has the lowest energy?

$$J = L + S, L + S - 1, \dots, |L - S|$$

$$J_{^3H} = 6, 5, 4$$

So the ground state terms are

$$^3H_6, ^3H_5, ^3H_4 \quad (2)$$

Because the shells are less than half-filled, the lowest energy term has the smallest value of J which is 3H_4 .

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17. List the term symbols for the Carbon atom ($1s^2 2s^2 2p^2$).

This example was worked in the notes; cf. Eqs. (3.137) and following. The terms are

$$^3P, ^1D, ^1S$$

18. Is

$$\Psi(\mathbf{r}_1, \sigma(1), \mathbf{r}_2, \sigma(2)) \propto e^{-\zeta r_1} e^{-\zeta r_2} (1 + b|\mathbf{r}_1 - \mathbf{r}_2| + c|\mathbf{r}_1 - \mathbf{r}_2|^2)(\alpha(1)\beta(2) + \alpha(2)\beta(1)) \quad (3)$$

an acceptable approximate wave function for the Helium atom?

No. This wave function is not antisymmetric. It would be OK if

$$\Psi(\mathbf{r}_1, \sigma(1), \mathbf{r}_2, \sigma(2)) \propto e^{-\zeta r_1} e^{-\zeta r_2} (1 + b|\mathbf{r}_1 - \mathbf{r}_2| + c|\mathbf{r}_1 - \mathbf{r}_2|^2)(\alpha(1)\beta(2) - \alpha(2)\beta(1))$$

19. Is $\Psi(\mathbf{r}_1, \sigma(1), \mathbf{r}_2, \sigma(2)) = \psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) \frac{(\alpha(1)\beta(2) - \alpha(2)\beta(1))}{\sqrt{2}}$ an acceptable wave

function for first singlet excited state of the Helium atom?

No. Electrons are indistinguishable particles. For this reason, we cannot “label” electron one as the “1s” electron and electron 2 as the “2s electron”. It would be OK if

$$\Psi(\mathbf{r}_1, \sigma(1), \mathbf{r}_2, \sigma(2)) = \frac{(\psi_{1s}(\mathbf{r}_1)\psi_{2s}(\mathbf{r}_2) + \psi_{1s}(\mathbf{r}_2)\psi_{2s}(\mathbf{r}_1))}{\sqrt{2}} \frac{(\alpha(1)\beta(2) - \alpha(2)\beta(1))}{\sqrt{2}}$$

20. Which of the following commutators are zero,

(a) $[\hat{H}, \hat{L}_x]$	(d) $[\hat{L}^2, \hat{L}_x]$	(g) $[\hat{J}^2, \hat{L}^2]$	(j) $[\hat{J}_z, \hat{L}_x]$
(b) $[\hat{H}, \hat{L}_z]$	(e) $[\hat{L}_x, \hat{L}_z]$	(h) $[\hat{H}, \hat{J}^2]$	(k) $[\hat{J}^2, \hat{S}_z]$
(c) $[\hat{H}, \hat{S}_x]$	(f) $[\hat{L}_x, \hat{S}_z]$	(i) $[\hat{J}_z, \hat{S}_z]$	(l) $[\hat{J}^2, \hat{J}_x]$

a, b, c, d, f, g, h, i, l. (e, j, and k are not zero.)

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

$$\Psi_{\zeta} \equiv \frac{1}{\sqrt{2}} |\psi_1 \alpha \ \psi_1 \beta| \quad (4)$$

where

$$\psi_1(\mathbf{r}) = \sqrt{\frac{\zeta^3}{\pi}} e^{-\zeta r}; \zeta > 0. \quad (5)$$

We have that

$$\begin{aligned} E(\zeta) &\equiv \frac{\left\langle \Psi_1 \left| \left(-\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right) \right| \Psi_1 \right\rangle}{\langle \Psi_1 | \Psi_1 \rangle} \\ &= -\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - 2) \end{aligned} \quad (6)$$

21. Write out the wave function that corresponds to the Slater determinant in Eq. (4). (3 points)

$$\Psi_{\zeta} \equiv \psi_1(\mathbf{r}_1) \psi_1(\mathbf{r}_2) \frac{\alpha(1)\beta(2) - \alpha(2)\beta(1)}{\sqrt{2}}$$

22. Using the Slater determinant in Eq. (4), what energy do you obtain if you perform the Hartree-Fock method with the orbitals given in Eq. (5). (2 points)

The Hartree-Fock method finds the lowest-energy Slater determinant of a given form. Since Eq. (6) is the energy expression, we need to find the value of ζ for which the energy is minimized. At the minimum, $\frac{\partial E}{\partial \zeta} = 0$. Thus

$$\begin{aligned} 0 &= \frac{\partial}{\partial \zeta} \left(-\zeta^2 + \frac{5}{8}\zeta + 2\zeta(\zeta - 2) \right) \\ &= -2\zeta + \frac{5}{8} + 4\zeta - 4 \\ &= 2\zeta - \frac{27}{8} \\ \zeta &= \frac{27}{16} = 1.6875 \end{aligned} \quad (7)$$

We substitute back into Eq. (6), and obtain

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

This problem was in the notes; cf. (3.22)-(3.28).

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Part 2. Hints are available if you need them. Partial credit will be given only if your work is show and neat.

1. We can express the wave function for a two-electron atom, $\Psi(r_1, r_2)$, as a function of $u \equiv r_1 - r_2$ and $v = r_1 + r_2$, $\Psi(u, v)$.

Consider the function

$$\Gamma(u) \equiv \int_0^{2\pi} \int_0^\pi \int \Psi^*(u, v) \Psi(u, v) dv d\theta_u d\phi_u \quad (9)$$

Here $u = |u|$, θ_u is the angle u forms with the z axis, etc.. (That is, we are writing u in spherical coordinates.)

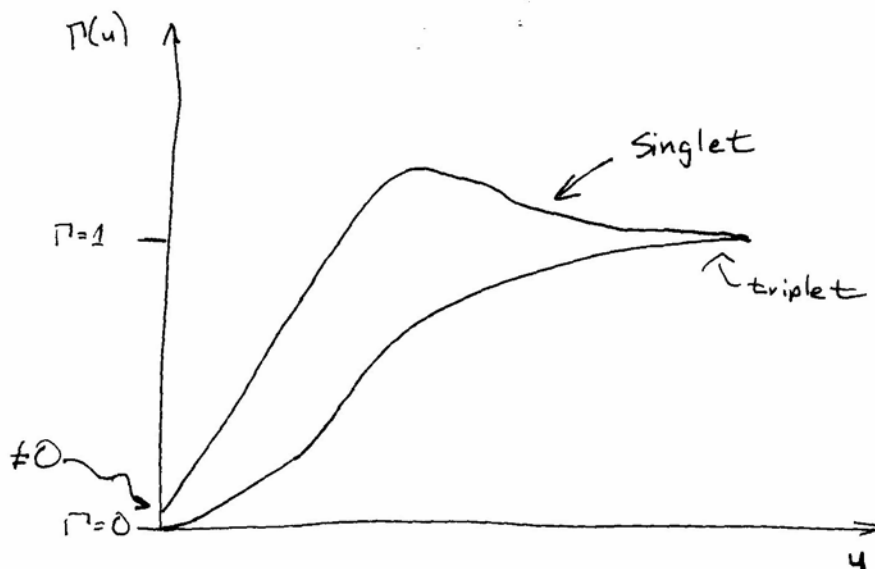
- (a) Plot $\Gamma(u)$ vs. u for a triplet state and a singlet state. If you know any specific values (e.g., $\Gamma(u=0)$ or $\Gamma(u \rightarrow \infty)$), write them on the graph. (3 points)

Hints:

1. $\Gamma(u)$ represents the probability that two electrons are some distance apart. E.g., if electron one is at (x, y, z) , $\Gamma(u)$ represents the probability electron 2 is at $(x, y, z + u)$.
2. The two electrons have the same spin in the triplet state, but not in the singlet state.

Solution: This problem tested the Pauli-exclusion principle. The probability of two same-spin electrons being close together is zero, and $\Gamma(u)$ is quadratic in the region of electron coalescence. The probability of two opposite-spin electrons being close together is small, but not quite zero.

When electrons are far apart, they are uncorrelated. So $\Psi(r_1, r_2) \rightarrow \Psi(r_1)\Psi(r_2)$. At this point, there is essentially no dependence of the wave function on $|r_1 - r_2|$ (this is most easily seen if we consider an exponential form, wherein $e^{-\alpha r_1} e^{-\alpha r_2} \rightarrow e^{-\alpha(r_1+r_2)}$). So $\Gamma(u \rightarrow \infty) = 1$. I decided this was a bit complicated, so I'm only grading the "small u " behavior (but I'm giving one bonus point to people who got the large u behavior correct).



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(b) Rychlewski has proposed that the wave function for the Helium atom be written as

$$\Psi_R(\mathbf{r}_1, \sigma(1); \mathbf{r}_2, \sigma(2)) = e^{-\zeta v} (1 - s \cdot e^{-\alpha u^2}) F(\theta_v, \phi_v; \theta_u, \phi_u) \quad (10)$$

Suppose one finds the parameters $\zeta, s, \lambda, \alpha$ and finds the function $F(\theta_v, \phi_v; \theta_u, \phi_u)$ for which the energy,

$$E_R \equiv \frac{\left\langle \Psi_R \left| -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \right| \Psi_R \right\rangle}{\langle \Psi_R | \Psi_R \rangle} \quad (11)$$

is minimized. Is E_R greater than, less than, or equal to the “exact” energy for the Helium atom? (By “exact” I mean the energy of the Helium atom in the Born-Oppenheimer approximation.) (3 points)

Hint: Think variational principle.

Solution: $E_R > E_{true}$, of course, because no “inexact” wave function, nomatter how good, will have an energy less than or equal to the that of the exact wave function.

2. (a) What is the value of the commutator, $[\hat{S}_x^2 + \hat{S}_y^2, S_z]$? (3 points)

Hint: Remember that $\hat{S}^2 = \hat{S}_x^2 + \hat{S}_y^2 + \hat{S}_z^2$.

Solution:

$$[\hat{S}_x^2 + \hat{S}_y^2, \hat{S}_z] = [\hat{S}^2 - \hat{S}_z^2, \hat{S}_z] = [\hat{S}^2, \hat{S}_z] - [\hat{S}_z^2, \hat{S}_z] = 0 - 0 = 0$$

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(b) The lowest energy term for the Chromium atom ($4s^1 3d^5$ configuration) is 7S .

Let Ψ_{τ_S} be one of the seven degenerate ground state wave functions for this term, and Ψ_{τ_S} is an eigenfunction of \hat{L}^2 , \hat{S}^2 , \hat{S}_z , and \hat{L}_z . For this particular state, one measures

$$\hat{S}_z \Psi_{\tau_S} = 2\hbar \Psi_{\tau_S} \quad (12)$$

Is this function an eigenvalue of $\hat{S}_x^2 + \hat{S}_y^2$? If so, what is its eigenvalue?

(3 points)

Hints:

The projection of the spin-angular momentum vector, $\hat{\mathbf{S}}$ onto the z -axis was $2\hbar$. How much “vector” is left over for the other directions.

$$\hat{S}^2 \Psi_i^{L,S,M_L,M_s} = \hbar^2 (S(S+1)) \Psi_i^{L,S,M_L,M_s}$$

Solution:

Yes, it is an eigenfunction. The eigenvalue is:

$$\begin{aligned} (\hat{S}_x^2 + \hat{S}_y^2) \Psi_i^{L,S,M_L,M_s} &= (\hat{S}^2 - \hat{S}_z^2) \Psi_i^{L,S,M_L,M_s} \\ &= \hat{S}^2 \Psi_i^{L,S,M_L,M_s} - \hat{S}_z^2 \Psi_i^{L,S,M_L,M_s} \\ &= \hbar^2 (S(S+1)) \Psi_i^{L,S,M_L,M_s} - \hat{S}_z (\hbar M_s) \Psi_i^{L,S,M_L,M_s} \\ &= \hbar^2 (S(S+1)) \Psi_i^{L,S,M_L,M_s} - (\hbar M_s)^2 \Psi_i^{L,S,M_L,M_s} \\ &= \hbar^2 (S(S+1) - M_s^2) \Psi_i^{L,S,M_L,M_s} \end{aligned}$$

Substitution gives the eigenvalue for the state here, with $S = 3$ and $M_s = 2$, as

$$\hbar^2 (S(S+1) - M_s^2) = \hbar^2 (3(4) - 2^2) = 8\hbar^2$$

This problem is the justification for the “cone diagrams” drawn in the notes. At any given “point in time”, one can specify the magnitude of the spin-angular momentum vector ($\hbar\sqrt{S(S+1)}$), the projection of the angular momentum on any axis of choice (we pick the z -axis, for convenience), $\hbar M_s$, and the “radius of the cone”, which is the amount of spin-angular momentum in the x and y directions, $\hbar\sqrt{S(S+1) - M_s^2}$. Note that even when $M_s = S$ (that is, all spins are parallel and pointed up), there is some (albeit rather small) projection of the spin-angular momentum onto the x - y plane.

Of course, since $[\hat{S}_x, \hat{S}_y] \neq 0$, we can't say exactly what S_x and S_y are. All we can say is that the spin-angular momentum has some component in these directions, with the total magnitude given by the solution to this problem.

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3. When we put a Hydrogen atom in an electric field in the x -direction and a magnetic field in the z -direction the Hamiltonian becomes

$$\hat{H}_{B,E} \equiv -\frac{1}{2}\nabla^2 - \frac{1}{r} + \left(1 + \frac{(j)(j+1)-l(l+1)+\frac{1}{2}(\frac{3}{2})}{2(j)(j+1)}\right) \frac{\beta_e B_z}{\hbar} \hat{J}_z + \mathcal{E}x \quad (13)$$

where, as expected, the states are split according to whether

$$\begin{aligned} j &= l + \frac{1}{2} \\ \text{or} \\ j &= l - \frac{1}{2} \end{aligned} \quad (14)$$

and $\hat{J}_z = \hat{L}_z + \hat{S}_z$.

(a) Calculate (5 points)

$$\begin{aligned} \hat{J}_z \psi_{1s}(\mathbf{r}_1) \alpha(1) &= \frac{\hbar}{2} \psi_{1s}(\mathbf{r}_1) \alpha(1) \\ \hat{J}_z \psi_{1s}(\mathbf{r}_1) \beta(1) &= -\frac{\hbar}{2} \psi_{1s}(\mathbf{r}_1) \beta(1) \\ \hat{J}_z \psi_{2p_{+1}}(\mathbf{r}_1) \alpha(1) &= \frac{3\hbar}{2} \psi_{2p_{+1}}(\mathbf{r}_1) \alpha(1) \\ \hat{J}_z \psi_{2p_{-1}}(\mathbf{r}_1) \alpha(1) &= -\frac{\hbar}{2} \psi_{2p_{-1}}(\mathbf{r}_1) \alpha(1) \\ \hat{J}_z \psi_{2p_0}(\mathbf{r}_1) \alpha(1) &= \frac{\hbar}{2} \psi_{2p_0}(\mathbf{r}_1) \alpha(1) \end{aligned} \quad (15)$$

Hint: $\hat{J}_z \psi_{n,l,m_l,m_s}(\mathbf{r}) = \hbar(m_l + m_s) \psi_{n,l,m_l,m_s}(\mathbf{r})$.

(b) In the absence of the electric field but the presence of the magnetic field, what is the ground-state energy and eigenfunction for the Hydrogen atom? (4 points)

Hint: Use result from part (a) in the Hamiltonian. $\psi_{1s}(\mathbf{r})\alpha(1)$ and $\psi_{1s}(\mathbf{r})\beta(1)$ are actually eigenfunctions of this Hamiltonian (in the absence of the electric field).

Solution:

Let's apply the Hamiltonian from Eq. (13) to the 1s orbital. We have

$$\begin{aligned} \hat{H}_{B,E} \psi_{1s}(\mathbf{r}_1) \begin{Bmatrix} \alpha(1) \\ \beta(1) \end{Bmatrix} &\equiv \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_1} + \left(1 + \frac{(j)(j+1)-l(l+1)+\frac{1}{2}(\frac{3}{2})}{2(j)(j+1)}\right) \frac{\beta_e B_z}{\hbar} \hat{J}_z(\mathbf{r}_1) \right) \psi_{1s}(\mathbf{r}_1) \begin{Bmatrix} \alpha(1) \\ \beta(1) \end{Bmatrix} \\ &= \left(-\frac{1}{2}\nabla_1^2 - \frac{1}{r_1} \right) \psi_{1s}(\mathbf{r}_1) \begin{Bmatrix} \alpha(1) \\ \beta(1) \end{Bmatrix} + \left(1 + \frac{(\frac{1}{2})(\frac{1}{2}+1)-0(0+1)+\frac{1}{2}(\frac{3}{2})}{2(\frac{1}{2})(\frac{1}{2}+1)}\right) \frac{\beta_e B_z}{\hbar} \left(\frac{\hbar}{2}\right) \psi_{1s}(\mathbf{r}_1) \begin{Bmatrix} 1 \cdot \alpha(1) \\ -1 \cdot \beta(1) \end{Bmatrix} \end{aligned} \quad (16)$$

where the first term is just the Hamiltonian for the isolated Hydrogen atom and we know that $j = \frac{1}{2}$ because $|l + s| = \frac{1}{2} = |l - s|$ when $l = 0$. Substituting in the energy of the Hydrogen atom ($-\frac{1}{2}$) and simplifying (and using atomic units, as needed), we obtain

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$$\begin{aligned}
\hat{H}_{B,E} \psi_{1s}(\mathbf{r}_1) \begin{Bmatrix} \alpha(1) \\ \beta(1) \end{Bmatrix} &\equiv \left(-\frac{1}{2} \nabla_1^2 - \frac{1}{r_1} \right) \psi_{1s}(\mathbf{r}_1) \begin{Bmatrix} \alpha(1) \\ \beta(1) \end{Bmatrix} \\
&+ \left(1 + \frac{(\frac{1}{2})(\frac{1}{2}+1) - 0(0+1) + \frac{1}{2}(\frac{3}{2})}{2(\frac{1}{2})(\frac{1}{2}+1)} \right) \frac{\beta_e B_z}{\hbar} \left(\frac{\hbar}{2} \right) \psi_{1s}(\mathbf{r}_1) \begin{Bmatrix} 1 \cdot \alpha(1) \\ -1 \cdot \beta(1) \end{Bmatrix} \\
&= \left(-\frac{1}{2} \right) \psi_{1s}(\mathbf{r}_1) \begin{Bmatrix} \alpha(1) \\ \beta(1) \end{Bmatrix} + \left(1 + \frac{2(\frac{1}{2})(\frac{3}{2})}{2(\frac{1}{2})(\frac{3}{2})} \right) \left(\frac{\beta_e B_z}{2} \right) \psi_{1s}(\mathbf{r}_1) \begin{Bmatrix} 1 \cdot \alpha(1) \\ -1 \cdot \beta(1) \end{Bmatrix} \\
&= \left(-\frac{1}{2} \pm \beta_e B_z \right) \psi_{1s}(\mathbf{r}_1) \begin{Bmatrix} \alpha(1) \\ \beta(1) \end{Bmatrix}
\end{aligned} \tag{17}$$

From this it follows that the ground state energy is $-\frac{1}{2} - \beta_e |B_z|$ and the ground state wave function is $\psi_{1s}(\mathbf{r}_1)\beta(1)$ if $B_z > 0$ and $\psi_{1s}(\mathbf{r}_1)\alpha(1)$ if $B_z < 0$. If $B_z = 0$, we have the unperturbed Hydrogen atom wave function and the two states are degenerate.

If you remembered Eq. (3.45) in the notes, there was no need to do much mathematics at all.

(c) We excite our atoms to the $n = 2$ state with a laser and then pass our atoms through a Stern-Gerlach apparatus and select only the $\psi_{2s}(\mathbf{r}_1)\alpha(1); \psi_{2p_{+1}}(\mathbf{r}_1)\beta(1);$ and $\psi_{2p_{-1}}(\mathbf{r}_1)\alpha(1)$ states. Next, we apply an electric field in the x -direction and a magnetic field in the z -direction. Using perturbation theory, estimate the energies and eigenvectors of these states. (4 points)

Solution:

All these states have a $j = \frac{1}{2}$ component--this is why I revised the problem thusly during the examination. (Of course, one can treat the case where there are different j 's.)

The first step of the "full" solution is to derive the perturbation matrix. To do this, we need to evaluate integrals like:

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$$\begin{aligned}
& \left\langle \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \left| \left(1 + \frac{(j)(j+1)-l(l+1)+\frac{1}{2}(\frac{3}{2})}{2(j)(j+1)} \right) \frac{\beta_e B_z}{\hbar} \hat{J}_z + \mathcal{E}x \right| \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \right\rangle \\
&= \left\langle \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \left| \left(1 + \frac{(\frac{1}{2})(\frac{1}{2}+1)-l(l+1)+\frac{1}{2}(\frac{3}{2})}{2(\frac{1}{2})(\frac{1}{2}+1)} \right) \frac{\beta_e B_z}{\hbar} \hat{J}_z \right| \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \right\rangle \\
&+ \left\langle \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \left| \mathcal{E}x \right| \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \right\rangle \\
&= \left\langle \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \left| \left(1 + 1 - \frac{2 \cdot l(l+1)}{3} \right) \frac{\beta_e B_z}{\hbar} \hat{J}_z \right| \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \right\rangle \\
&+ \left\langle \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \left| \mathcal{E}x \right| \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \right\rangle \\
&= 2 \left\langle \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \left| \left(1 - \frac{l(l+1)}{3} \right) \frac{\beta_e B_z}{\hbar} \hat{J}_z \right| \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \right\rangle \\
&+ \left\langle \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \left| \mathcal{E}x \right| \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \right\rangle
\end{aligned} \tag{18}$$

I've shown a lot more steps here than necessary.

Using the appropriate values for the integrals, we obtain the matrix,

Name:

$$\begin{aligned}
& \left\langle \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p-1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p+1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \middle| \hat{V} \middle| \begin{bmatrix} \psi_{2s}(\mathbf{r}_1)\alpha(1) \\ \psi_{2p-1}(\mathbf{r}_1)\beta(1) \\ \psi_{2p+1}(\mathbf{r}_1)\alpha(1) \end{bmatrix} \right\rangle \\
& \begin{bmatrix} \langle \psi_i | \hat{V} | \psi_j \rangle & \psi_{2s}(\mathbf{r}_1)\alpha(1) & \psi_{2p+1}(\mathbf{r}_1)\beta(1) & \psi_{2p-1}(\mathbf{r}_1)\alpha(1) \\ \psi_{2s}(\mathbf{r}_1)\alpha(1) & \beta_e B_z & -\frac{3}{\sqrt{2}}\mathcal{E} & -\frac{3}{\sqrt{2}}\mathcal{E} \\ \psi_{2p+1}(\mathbf{r}_1)\beta(1) & -\frac{3}{\sqrt{2}}\mathcal{E} & -\frac{1\beta_e B_z}{3} & 0 \\ \psi_{2p-1}(\mathbf{r}_1)\alpha(1) & -\frac{3}{\sqrt{2}}\mathcal{E} & 0 & +\frac{1\beta_e B_z}{3} \end{bmatrix} \\
& \equiv \\
& = \begin{bmatrix} 3B & \varepsilon & \varepsilon \\ \varepsilon & -B & 0 \\ \varepsilon & 0 & B \end{bmatrix}
\end{aligned} \tag{19}$$

where $B = \frac{\beta_e B_z}{3}$ and $\varepsilon = -\frac{3}{\sqrt{2}}\mathcal{E}$.

Next, we need to evaluate the determinant,

$$\begin{vmatrix} 3B - \lambda & \varepsilon & \varepsilon \\ \varepsilon & -B - \lambda & 0 \\ \varepsilon & 0 & B - \lambda \end{vmatrix} = 0$$

$$\varepsilon(0 - \varepsilon(-B - \lambda)) + (B - \lambda)((3B - \lambda)(-B - \lambda) - \varepsilon^2) = 0 \tag{20}$$

$$-\lambda^3 + (2B + B)\lambda^2 + (\varepsilon^2 + \varepsilon^2 - 3B^2 - 2B^2)\lambda + \varepsilon^2 B - \varepsilon^2 B - 3B^3 = 0$$

This is difficult (but not impossible) to solve, so I told you to assume $B_z = 0$ and then find the eigenvalues and ground-state eigenvector. In this case,

$$-\lambda^3 + (2B + B)\lambda^2 + (\varepsilon^2 + \varepsilon^2 - 3B^2 - 2B^2)\lambda + \varepsilon^2 B - \varepsilon^2 B - 3B^3 = 0$$

$$-\lambda^3 + 0 + 2\varepsilon^2\lambda = 0 \tag{21}$$

$$\lambda(\lambda^2 - 2\varepsilon^2) = 0$$

$$\lambda = \pm\sqrt{2}|\varepsilon|$$

The eigenvalues are then $E = \frac{-1}{2(2)^2} \pm \sqrt{2} \left| -\frac{3}{\sqrt{2}}\mathcal{E} \right|$.

$$= \frac{-1}{8} \pm 3|\mathcal{E}|$$

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The ground state eigenvector is obtained by solving

$$\begin{bmatrix} \mp\sqrt{2}|\varepsilon| & |\varepsilon| & |\varepsilon| \\ |\varepsilon| & \mp\sqrt{2}|\varepsilon| & 0 \\ |\varepsilon| & 0 & \mp\sqrt{2}|\varepsilon| \end{bmatrix} \begin{bmatrix} c_{2s} \\ c_{-1} \\ c_{+1} \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix} \quad (22)$$

The last equation gives

$$\begin{aligned} \varepsilon c_{2s} \mp \sqrt{2}\varepsilon c_{+1} &= 0 \\ c_{2s} &= \pm\sqrt{2}c_{+1} \end{aligned} \quad (23)$$

The second equation gives

$$c_{2s} = \pm\sqrt{2}c_{-1} \quad (24)$$

and the third equation is redundant. We have, then, that

$$\psi_{\pm\sqrt{2}\varepsilon} = \pm\sqrt{2}\psi_{2s}(\mathbf{r}) + \psi_{2p_{-1}}(\mathbf{r}) + \psi_{2p_{+1}}(\mathbf{r}) \quad (25)$$

which can be normalized, if you like.

4. Recall that the energy of the first excited state can be found by minimizing the energy with respect to all wave functions that are orthogonal to the ground state, that is,

$$E_1 = \min_{\{\Psi|\langle\Psi|\Psi_0\rangle\}} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad (26)$$

where \hat{H} is the Hamiltonian of the system of interest, Ψ_0 is the ground state wave function for this system. The wave function one finds at the minimum point, that is, the ARGUMENT of the energy at the minimum, is the exact wave function for the first excited state:

$$\Psi_1 = \arg \min_{\{\Psi|\langle\Psi|\Psi_0\rangle\}} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}. \quad (27)$$

The problem with this method is that one must know the ground state wave function first. What if we are only interested in the excited state? It would be much better to have a method for finding this directly.

- (a) A recent paper, submitted to the Journal of Chemical Physics, proposed that

$$E_1 = \min_{\{\Psi|\Psi \text{ has a node}\}} \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} \quad (28)$$

that is, they have proposed that if we minimize the energy with respect to all wave functions that have exact one node, the energy of the first excited state is found. Is this true? Explain. (3 points)

Hint: Consider the wave function $\psi_{1s}(\mathbf{r}) + \varepsilon\psi_{2s}(\mathbf{r})$ where ε is small.

Solution: Just because the wave function has a node does not mean it is orthogonal to the ground state. Moreover, if we consider the (normalized) wave function, $\sqrt{1-\varepsilon^2}\psi_{1s}(\mathbf{r}) + \varepsilon\psi_{2s}(\mathbf{r})$, this wave function has an energy $E_{1s} + \varepsilon^2(E_{2s} - E_{1s}) < E_{2s}$ but this wave function has a node where

Name:

$$\begin{aligned}
0 &= \sqrt{1 - \varepsilon^2} \psi_{1s}(\mathbf{r}) + \varepsilon \psi_{2s}(\mathbf{r}) \\
&= \sqrt{1 - \varepsilon^2} \left(\sqrt{\frac{Z^3}{\pi}} \cdot e^{-Zr} \right) + \varepsilon \left(\sqrt{\frac{Z^3}{2^5 \pi}} \cdot (2 - Zr) e^{-Zr/2} \right) \\
&= 4\sqrt{2} \sqrt{1 - \varepsilon^2} e^{-Zr} + \varepsilon (2 - Zr) e^{-Zr/2} \\
&= 4\sqrt{2} \sqrt{1 - \varepsilon^2} + \varepsilon (2 - Zr) e^{Zr/2}
\end{aligned} \tag{29}$$

To see this very explicitly, note that this function is positive for small r but is negative as $r \rightarrow \infty$, and so this wave function has a node but has an energy less than the energy of the first excited state.

(b) Back in 1953, Pólya and Schiffer, extending earlier work by Poincare and Fischer, showed that the energy of the $(k-1)^{st}$ excited state can be obtained by a nested minimization wherein first one writes a wave function as a sum of k -linearly independent wave functions, $\{\Phi_i\}_{i=1}^k$,

$$\Psi \equiv \sum_{i=1}^k c_k \Phi_k \tag{30}$$

and then maximizes the energy with respect to the coefficients, c_k (inner loop) and minimizes the energy with respect to the choices for Φ_k (outer loop).

That is,

$$E_{k-1} \equiv \underbrace{\min}_{\{\Phi_i\}_{i=1}^k} \underbrace{\max}_{\Psi \equiv \sum_{i=1}^k c_k \Phi_k} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{31}$$

This is a not very hard to show, but we'll only worry about the first excited state.

Write the wave function as

$$\Psi = a\Phi_1 + b\Phi_2 \tag{32}$$

and show that

$$E_1 \equiv \underbrace{\min}_{\Phi_1, \Phi_2} \underbrace{\max}_{\Psi \equiv a\Phi_1 + b\Phi_2} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} \tag{33}$$

where Φ_1 is *not* proportional to Φ_2 . (7 points).

Hint: Write the wave functions as $\Phi_{1,2} = \sum_{i=0}^{\infty} c_i^{(1,2)} \Psi_i$, where Ψ_i is an eigenfunction of the Hamiltonian. Consider the inner minimization first.

Solution:

I allowed you to make some simplifying assumptions here, notably that $\langle \Phi_1 | \Phi_2 \rangle = 0$ and that $\Phi_1 = \Psi_0$, the ground state wave function. Here I'll show you how to work it through in "full detail", without the assumptions. This is the "right way" to work this problem, and I'd have been *very* pleased if someone did it this way. It is, provided you really *understand* what is going on, not that difficult.

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First, we need to think about what we are doing. We are expanding Ψ in a basis set of two functions, Φ_1 and Φ_2 and, for the same reason we could choose the eigenfunctions of the Hamiltonian to be orthogonal and normalized (cf. Problem set 1), we can choose Φ_1 and Φ_2 to be orthogonal and normalized. In mathematical parlance, the set of all wave functions that can be written as a linear combination of Φ_1 and Φ_2 is a two-dimensional “subspace”.

Now, we want to find the highest and lowest possible energy we can obtain from these states. To do this, remember that the lowest-possible energy is associated with the ground state eigenvalue of the Hamiltonian. Similarly, the highest possible energy is the largest eigenvalue of the Hamiltonian. So what we need to do is find the eigenfunctions of

$$\begin{bmatrix} \langle \Phi_1 | \hat{H} | \Phi_1 \rangle & \langle \Phi_1 | \hat{H} | \Phi_2 \rangle \\ \langle \Phi_2 | \hat{H} | \Phi_1 \rangle & \langle \Phi_2 | \hat{H} | \Phi_2 \rangle \end{bmatrix}$$

We define $\varepsilon_i = \langle \Phi_i | \hat{H} | \Phi_i \rangle$ and $\beta = \langle \Phi_2 | \hat{H} | \Phi_1 \rangle = \langle \Phi_1 | \hat{H} | \Phi_2 \rangle^*$ and so, if we find the eigenvalues, we obtain

$$E = \frac{\varepsilon_1 + \varepsilon_2}{2} \pm \frac{(\varepsilon_1 - \varepsilon_2)}{2} \sqrt{1 + \frac{4|\beta|^2}{(\varepsilon_1 - \varepsilon_2)^2}} \quad (34)$$

The particular form of the formula is not important, but you should recall that it is the same formula we found when we looked at molecules: when two states come together, the “higher energy state” goes up in energy and the “lower energy state” goes down in energy unless

$$\beta = \langle \Phi_2 | \hat{H} | \Phi_1 \rangle = 0,$$

which generally occurs, for example, when the “trial functions”, Φ_1, Φ_2 are eigenfunctions of the Hamiltonian, $\hat{H}\Phi_i = E_i\Phi_i$.

The result of the “inner maximization” in Eq. (33) is, from this analysis,

$$\max_{\Psi \equiv a\Phi_1 + b\Phi_2} \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle} = \frac{\varepsilon_1 + \varepsilon_2}{2} - \frac{(\varepsilon_1 - \varepsilon_2)}{2} \sqrt{1 + \frac{4|\beta|^2}{(\varepsilon_1 - \varepsilon_2)^2}}$$

if $\varepsilon_2 > \varepsilon_1$. All the preceding is unnecessary—I would have been happy (though surprised) if you just told me that your remembered from linear algebra that the maximum value of the quadratic form (LHS of the preceding equation) was equal to the largest eigenvalue of the matrix (RHS of the equation).

Now, how do you make the RHS as small as possible. Clearly we should choose Φ_1 and Φ_2 so that $\beta = 0$ —this is always beneficial. That is, we want the largest eigenvalue of the matrix to be equal to ε_2 . Moreover, so we need to find orthogonal functions, Φ_1 and Φ_2 , such that $\varepsilon_1 < \varepsilon_2$ but ε_2 is as small as zero. What functions do the trick? Well, if we choose ε_1 to be small, that is good (it lets ε_2 be smaller since we have required $\varepsilon_2 > \varepsilon_1$). So we should let ε_1 be the ground state energy. Then, we need to minimize the energy of Φ_2 , ε_2 , subject to the constraint that the wave function is orthogonal to the ground state. Wait a second, that is just the “usual way” to find excited states. So the Poincare-Fischer method must be just a fancy-schmancy way of restating the excited-state variational principle.

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Now this seems long, but if I was going to write it out, I'd have just said:

Give me a subspace of dimension 2. Now, find the largest eigenvalue of the Hamiltonian projected on that subspace. This energy is greater than or equal to the energy of the first excited state because:

- (a) If the subspace spans the space of the first 2 eigenstates, then the energy = first excited state energy. That is, if $\Phi_i = c_0^{(i)}\Psi_0 + c_1^{(i)}\Psi_1$, then there is no “component” in the wave function of a higher-energy state, so the largest possible energy you can construct with these wavefunctions is that of the first excited state. Moreover, you can always construct the first excited state since Φ_1 and Φ_2 are linearly independent
- (b) If case (a) does not hold, then the subspace must have some component of one of the higher eigenstates. (That is, $\Phi_i = c_0^{(i)}\Psi_0 + c_1^{(i)}\Psi_1 + \sum_{k=2}^{\infty} c_k^{(i)}\Psi_k$, and not all of the $\{c_k^{(i)}\}_{k=2}^{\infty}$ are equal to zero.) In this case, the subspace has some component from a higher energy state, so the highest possible energy that you can construct from Φ_1 and Φ_2 will have a contribution from the high-energy state, so that the maximum energy you can construct will be greater than the first excited state energy.

So maximizing the energy with respect to $\Psi = b_1\Phi_1 + b_2\Phi_2$ gives an energy greater than the first excited state energy (case (b)) unless $\Phi_i = c_0^{(i)}\Psi_0 + c_1^{(i)}\Psi_1$ (case (a)). So if we minimize the “maximum energy” with respect to the choice of Φ_1, Φ_2 , we'll obtain $\Phi_i = c_0^{(i)}\Psi_0 + c_1^{(i)}\Psi_1$ (case (a)) and the energy will be the energy of the first excited state.

This is a classic case where you “know everything you need to know” but you have to pull a lot of disparate information together. Of course, that is the art of science (an incongruous statement if ever there was one).

Name:

Formulae for Reference:

$$\begin{aligned}
\psi_{1s}(\mathbf{r}) &= \Psi_{1,0,0}(\mathbf{r}) = \sqrt{\frac{Z^3}{\pi}} \cdot e^{-Zr} \\
\psi_{2s}(\mathbf{r}) &= \Psi_{2,0,0}(\mathbf{r}) = \sqrt{\frac{Z^3}{2^5 \pi}} \cdot (2 - Zr) e^{-Zr/2} \\
\psi_{2p_0}(\mathbf{r}) &= \Psi_{2,1,0}(\mathbf{r}) = \sqrt{\frac{Z^3}{2^5 \pi}} \cdot (Zr) e^{-Zr/2} Y_1^0(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{2^5 \pi}} \cdot (Zr) e^{-Zr/2} \cos(\theta) \\
\psi_{2p_{\pm 1}}(\mathbf{r}) &= \Psi_{2,1,\pm 1}(\mathbf{r}) = \sqrt{\frac{Z^3}{2^6 \pi}} \cdot (Zr) e^{-Zr/2} Y_1^{\pm 1}(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{2^6 \pi}} \cdot (Zr) e^{-Zr/2} \sin(\theta) e^{\pm i\phi} \\
\psi_{3s}(\mathbf{r}) &= \Psi_{3,0,0}(\mathbf{r}) = \sqrt{\frac{Z^3}{3^9 \pi}} \cdot (27 - 18Zr + 2(Zr)^2) e^{-Zr/3} \\
\psi_{3p_0}(\mathbf{r}) &= \Psi_{3,1,0}(\mathbf{r}) = \sqrt{\frac{2Z^3}{3^8 \pi}} \cdot (Zr)(6 - Zr) e^{-Zr/3} Y_1^0(\theta, \phi) \\
&= \sqrt{\frac{2Z^3}{3^8 \pi}} \cdot (Zr)(6 - Zr) e^{-Zr/3} \cos(\theta) \\
\psi_{3p_{\pm 1}}(\mathbf{r}) &= \Psi_{3,1,\pm 1}(\mathbf{r}) = \sqrt{\frac{Z^3}{3^8 \pi}} \cdot (Zr)(6 - Zr) e^{-Zr/3} Y_1^{\pm 1}(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{3^8 \pi}} \cdot (Zr)(6 - Zr) e^{-Zr/3} \sin(\theta) e^{\pm i\phi} \\
\psi_{3d_0}(\mathbf{r}) &= \Psi_{3,2,0}(\mathbf{r}) = \sqrt{\frac{Z^3}{2 \cdot 3^5 \pi}} \cdot (Zr)^2 e^{-Zr/3} Y_2^0(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{2 \cdot 3^5 \pi}} \cdot (Zr)^2 e^{-Zr/3} (3 \cos^2(\theta) - 1) \\
\psi_{3d_{\pm 1}}(\mathbf{r}) &= \Psi_{3,2,\pm 1}(\mathbf{r}) = \sqrt{\frac{Z^3}{3^4 \pi}} \cdot (Zr)^2 e^{-Zr/3} Y_2^{\pm 1}(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{3^4 \pi}} \cdot (Zr)^2 e^{-Zr/3} \sin(\theta) \cos(\theta) e^{\pm i\phi} \\
\psi_{3d_{\pm 2}}(\mathbf{r}) &= \Psi_{3,2,\pm 2}(\mathbf{r}) = \sqrt{\frac{Z^3}{2 \cdot 3^4 \pi}} \cdot (Zr)^2 e^{-Zr/3} Y_2^{\pm 2}(\theta, \phi) \\
&= \sqrt{\frac{Z^3}{4 \cdot 3^4 \pi}} \cdot (Zr)^2 e^{-Zr/3} \sin^2(\theta) e^{\pm 2i\phi}
\end{aligned}$$

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We define

$$\left\langle \psi_{2s}(\mathbf{r}) | x | \psi_{2p_{\pm 1}}(\mathbf{r}) \right\rangle = V_{2s, 2p_{\pm 1}} \quad (35)$$

and similarly for the other orbitals. Then:

$$V_{2s, 2s} = V_{2p_{+1}, 2p_{-1}} = V_{2p_{\pm 1}, 2p_{\pm 1}} = 0 \quad (36)$$

$$V_{2s, 2p_{\pm 1}} = -\frac{3}{\sqrt{2}} \quad (.37)$$