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.

$$\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\left(-\frac{\nabla^2_{R_1}}{2M_1}-\frac{\nabla^2_{R_2}}{2M_2}\right)\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)-\frac{\nabla_{R_1}\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\cdot\nabla_{R_1}\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)}{M_1}$$

$$-\frac{\nabla_{R_2}\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\cdot\nabla_{R_2}\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)}{M_2}+\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)\left(-\frac{\nabla^2_{R_1}}{2M_1}-\frac{\nabla^2_{R_2}}{2M_2}\right)\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)$$

$$+\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\left(-\frac{\nabla^2_{r_1}}{2}-\frac{\nabla^2_{r_2}}{2}+\frac{Z_1Z_2}{|\boldsymbol{R}_1-\boldsymbol{R}_2|}-\frac{Z_1}{|\boldsymbol{r}_1-\boldsymbol{R}_1|}-\frac{Z_2}{|\boldsymbol{r}_1-\boldsymbol{R}_2|}-\frac{Z_1}{|\boldsymbol{r}_2-\boldsymbol{R}_1|}-\frac{Z_2}{|\boldsymbol{r}_2-\boldsymbol{R}_2|}+\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\right)\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)$$

$$=E\chi_n\left(\boldsymbol{R}_1,\boldsymbol{R}_2\right)\psi_e\left(\boldsymbol{r}_1,\boldsymbol{r}_2;\boldsymbol{R}_1,\boldsymbol{R}_2\right)$$

2. Using the following definitions,

$$\hat{T}_e\equiv-\frac{\nabla^2_{r_1}}{2}-\frac{\nabla^2_{r_2}}{2}\qquad\qquad\hat{T}_n\equiv-\frac{\nabla^2_{R_1}}{2M_1}-\frac{\nabla^2_{R_2}}{2M_2}$$

$$\hat{V}_{ee}\equiv\frac{1}{|\boldsymbol{r}_1-\boldsymbol{r}_2|}\qquad\qquad\hat{V}_{nn}\equiv\frac{Z_1Z_2}{|\boldsymbol{R}_1-\boldsymbol{R}_2|}$$

$$\hat{V}_{ne}\equiv-\frac{Z_1}{|\boldsymbol{r}_1-\boldsymbol{R}_1|}-\frac{Z_2}{|\boldsymbol{r}_1-\boldsymbol{R}_2|}-\frac{Z_1}{|\boldsymbol{r}_2-\boldsymbol{R}_1|}-\frac{Z_2}{|\boldsymbol{r}_2-\boldsymbol{R}_2|}$$

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

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

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

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

_____ Hartree   _____ Hertz   _____ kJ/mol

_____ electron volt   ____ 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.

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

_____   **a.   In atomic units**

_____   **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) $l = 0, 1, 2, \ldots, n$
(b) $l = 1, 2, \ldots, n$
(c) $l = 0, 1, 2, \ldots, n-1$
(d) $l = 1, 2, \ldots, n-1$
(e) $-n, -n+1, \ldots, n-1, n$
(f) $-n+1, -n+2 \ldots, n-2, n-1$
(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

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 $r \to \infty$.

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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.**

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!!)**

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.**

$$\psi_{n,l,m}(r,\theta,\phi) \propto$$

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*
$2p_x$			
$4s$			
$6f_{z(2z^2-3x^2-3y^2)}$			

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

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

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

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

18. **Is**

$$\Psi\left(r_1, \sigma\left(1\right), r_2, \sigma\left(2\right)\right) \propto e^{-\zeta r_1} e^{-\zeta r_2} \left(1 + b\left|r_1 - r_2\right| + c\left|r_1 - r_2\right|^2\right)\left(\alpha\left(1\right)\beta\left(2\right) + \alpha\left(2\right)\beta\left(1\right)\right) \qquad (1)$$

an acceptable approximate wave function for the Helium atom?

19. **Is** $\Psi\left(r_1, \sigma\left(1\right), r_2, \sigma\left(2\right)\right) = \psi_{1s}\left(r_1\right)\psi_{2s}\left(r_2\right)\dfrac{\left(\alpha\left(1\right)\beta\left(2\right) - \alpha\left(2\right)\beta\left(1\right)\right)}{\sqrt{2}}$ **an acceptable wave**

function for first singlet excited state of the Helium atom?

20. **Which of the following commutators are zero,**

(a) $\left[\hat{H}, \hat{L}_x\right]$ **(d)** $\left[\hat{L}^2, \hat{L}_x\right]$ **(g)** $\left[\hat{J}^2, \hat{L}^2\right]$ **(j)** $\left[\hat{J}_z, \hat{L}_x\right]$

(b) $\left[\hat{H}, \hat{L}_z\right]$ **(e)** $\left[\hat{L}_x, \hat{L}_z\right]$ **(h)** $\left[\hat{H}, \hat{J}^2\right]$ **(k)** $\left[\hat{J}^2, \hat{S}_z\right]$

(c) $\left[\hat{H}, \hat{S}_x\right]$ **(f)** $\left[\hat{L}_x, \hat{S}_z\right]$ **(i)** $\left[\hat{J}_z, \hat{S}_z\right]$ **(l)** $\left[\hat{J}^2, \hat{J}_x\right]$

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

$$\Psi_\zeta \equiv \tfrac{1}{\sqrt{2}} \left| \psi_1 \alpha \ \psi_1 \beta \right| \tag{2}$$

where

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

We have that

$$
E(\zeta) \equiv \frac{\left\langle \Psi_1 \left| \left| -\dfrac{\nabla_1^2}{2} - \dfrac{\nabla_2^2}{2} - \dfrac{2}{r_1} - \dfrac{2}{r_2} + \dfrac{1}{|\boldsymbol{r}_1 - \boldsymbol{r}_2|} \right| \right| \Psi_1 \right\rangle}{\left\langle \Psi_1 \middle| \Psi_1 \right\rangle}
$$
$$
= -\zeta^2 + \tfrac{5}{8}\zeta + 2\zeta(\zeta - 2) \tag{4}
$$

21. Write out the wave function that corresponds to the Slater determinant in Eq. (2). (3 points)

22. Using the Slater determinant in Eq. (2), what energy do you obtain if you perform the Hartree-Fock method with the orbitals given in Eq. (3). (2 points)

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

$$\Gamma(u) \equiv \int_0^{2\pi} \int_0^{\pi} \int \Psi^*(u, v)\Psi(u, v)\,dvd\theta_u\phi_u \tag{5}$$

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 $\Gamma(u \to \infty)$), write them on the graph. (3 points)

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

$$\Psi_R(r_1, \sigma(1); r_2, \sigma(2)) = e^{-\zeta v}\left(1 - s \cdot e^{-\alpha u^2}\right)F(\theta_v, \phi_v; \theta_u, \phi_u) \tag{6}$$

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,

$$E_R \equiv \frac{\left\langle \Psi_R \left| -\frac{\nabla_1^2}{2} - \frac{\nabla_2^2}{2} - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{|r_1 - r_2|} \right| \Psi_R \right\rangle}{\langle \Psi_R | \Psi_R \rangle} \tag{7}$$

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)

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

(b) **The lowest energy term for the Chromium atom ($4s^1 3d^5$ configuration) is ^7S. Let $\Psi_{^7S}$ be one of the seven degenerate ground state wave functions for this term, and $\Psi_{^7S}$ is an eigenfunction of $\hat{L}^2$, $\hat{S}^2$, $\hat{S}_z$, and $\hat{L}_z$. For this particular state, one measures**

$$\hat{S}_z \Psi_{^7S} = 2\hbar \Psi_{^7S} \tag{8}$$

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

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**

$$\hat{H}_{B,E} \equiv -\frac{1}{2}\nabla^2 - \frac{1}{r} + \left(1 + \frac{(j)(j+1)-l(l+1)+\frac{1}{2}\left(\frac{3}{2}\right)}{2(j)(j+1)}\right)\frac{\beta_e B_z}{\hbar}\hat{J}_z + \mathcal{E}x \tag{9}$$

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

$$\begin{aligned} j &= l + \tfrac{1}{2} \\ &\text{or} \\ j &= l - \tfrac{1}{2} \end{aligned} \tag{10}$$

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

(a) **Calculate (5 points)**

$$\hat{J}_z \psi_{1s}\left(\boldsymbol{r}_1\right)\alpha\left(1\right) =$$

$$\hat{J}_z \psi_{1s}\left(\boldsymbol{r}_1\right)\beta\left(1\right) =$$

$$\hat{J}_z \psi_{2p_{+1}}\left(\boldsymbol{r}_1\right)\alpha\left(1\right) = \tag{11}$$

$$\hat{J}_z \psi_{2p_{-1}}\left(\boldsymbol{r}_1\right)\alpha\left(1\right) =$$

$$\hat{J}_z \psi_{2p_0}\left(\boldsymbol{r}_1\right)\alpha\left(1\right) =$$

(b) **In the presence of this magnetic field, what is the ground-state eigenvalue and eigenfunction for the Hydrogen atom? (4 points)**

(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 those atoms with $m_s = \frac{1}{2}$ and either $m_l = \pm 1$ or $l = 0$. That is, only the states described by $\psi_{2s}\left(r_1\right)\alpha\left(1\right); \psi_{2p_{+1}}\left(r_1\right)\alpha\left(1\right);$ and $\psi_{2p_{-1}}\left(r_1\right)\alpha\left(1\right)$ remain in our system. 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. Choose $j = \frac{3}{2}$. (4 points)**

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,

$$E_1 = \underbrace{\min}_{\{\Psi | \langle \Psi | \Psi_0 \rangle\}} \frac{\left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle}{\langle \Psi | \Psi \rangle} \tag{12}$$

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:

$$\Psi_1 = \arg \underbrace{\min}_{\{\Psi | \langle \Psi | \Psi_0 \rangle\}} \frac{\left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle}{\langle \Psi | \Psi \rangle}. \tag{13}$$

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

$$E_1 = \underbrace{\min}_{\{\Psi | \Psi \text{ has a node}\}} \frac{\left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle}{\langle \Psi | \Psi \rangle} \tag{14}$$

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)**

(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, $\{\Phi_i\}_{i=1}^{k}$,

$$\Psi \equiv \sum_{i=1}^{k} c_k \Phi_k \tag{15}$$

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,

$$E_{k-1} \equiv \underbrace{\min}_{\{\Phi_i\}_{i=1}^{k}} \underbrace{\max}_{\Psi \equiv \sum_{i=1}^{k} c_k \Phi_k} \frac{\left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle}{\langle \Psi | \Psi \rangle} \tag{16}$$

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

Write the wave function as

$$\Psi = a\Phi_1 + b\Phi_2 \tag{17}$$

and show that

$$E_1 \equiv \underbrace{\min}_{\Phi_1, \Phi_2} \underbrace{\max}_{\Psi \equiv a\Phi_1 + b\Phi_2} \frac{\left\langle \Psi \left| \hat{H} \right| \Psi \right\rangle}{\langle \Psi | \Psi \rangle} \tag{18}$$

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

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Formulae for Reference:

$$\psi_{1s}\left(\boldsymbol{r}\right) = \Psi_{1,0,0}\left(\boldsymbol{r}\right) = \sqrt{\frac{Z^3}{\pi}} \cdot e^{-Zr}$$

$$\psi_{2s}\left(\boldsymbol{r}\right) = \Psi_{2,0,0}\left(\boldsymbol{r}\right) = \sqrt{\frac{Z^3}{2^5\,\pi}} \cdot \left(2 - Zr\right) e^{-Zr/2}$$

$$\psi_{2p_0}\left(\boldsymbol{r}\right) = \Psi_{2,1,0}\left(\boldsymbol{r}\right) = \sqrt{\frac{Z^3}{2^5\,\pi}} \cdot (Zr)\,e^{-Zr/2}Y_1^0\left(\theta,\phi\right)$$

$$= \sqrt{\frac{Z^3}{2^5\,\pi}} \cdot (Zr)\,e^{-Zr/2}\cos\left(\theta\right)$$

$$\psi_{2p_{\pm1}}\left(\boldsymbol{r}\right) = \Psi_{2,1,\pm1}\left(\boldsymbol{r}\right) = \sqrt{\frac{Z^3}{2^6\,\pi}} \cdot (Zr)\,e^{-Zr/2}Y_1^{\pm1}\left(\theta,\phi\right)$$

$$= \sqrt{\frac{Z^3}{2^6\,\pi}} \cdot (Zr)\,e^{-Zr/2}\sin\left(\theta\right)e^{\pm i\phi}$$

$$\psi_{3s}\left(\boldsymbol{r}\right) = \Psi_{3,0,0}\left(\boldsymbol{r}\right) = \sqrt{\frac{Z^3}{3^9\,\pi}} \cdot \left(27 - 18Zr + 2(Zr)^2\right)e^{-Zr/3}$$

$$\psi_{3p_0}\left(\boldsymbol{r}\right) = \Psi_{3,1,0}\left(\boldsymbol{r}\right) = \sqrt{\frac{2Z^3}{3^8\,\pi}} \cdot (Zr)(6 - Zr)\,e^{-Zr/3}Y_1^0\left(\theta,\phi\right)$$

$$= \sqrt{\frac{2Z^3}{3^8\,\pi}} \cdot (Zr)(6 - Zr)\,e^{-Zr/3}\cos\left(\theta\right)$$

$$\psi_{3p_{\pm1}}\left(\boldsymbol{r}\right) = \Psi_{3,1,\pm1}\left(\boldsymbol{r}\right) = \sqrt{\frac{Z^3}{3^8\,\pi}} \cdot (Zr)(6 - Zr)\,e^{-Zr/3}Y_1^{\pm1}\left(\theta,\phi\right)$$

$$= \sqrt{\frac{Z^3}{3^8\,\pi}} \cdot (Zr)(6 - Zr)\,e^{-Zr/3}\sin\left(\theta\right)e^{\pm i\phi}$$

$$\psi_{3d_0}\left(\boldsymbol{r}\right) = \Psi_{3,2,0}\left(\boldsymbol{r}\right) = \sqrt{\frac{Z^3}{2\cdot3^5\,\pi}} \cdot (Zr)^2\,e^{-Zr/3}Y_1^0\left(\theta,\phi\right)$$

$$= \sqrt{\frac{Z^3}{2\cdot3^9\,\pi}} \cdot (Zr)^2\,e^{-Zr/3}\left(3\cos^2\left(\theta\right) - 1\right)$$

$$\psi_{3d_{\pm1}}\left(\boldsymbol{r}\right) = \Psi_{3,2,\pm1}\left(\boldsymbol{r}\right) = \sqrt{\frac{Z^3}{3^4\,\pi}} \cdot (Zr)^2\,e^{-Zr/3}Y_1^{\pm1}\left(\theta,\phi\right)$$

$$= \sqrt{\frac{Z^3}{3^8\,\pi}} \cdot (Zr)^2\,e^{-Zr/3}\sin\left(\theta\right)\cos\left(\theta\right)e^{\pm i\phi}$$

$$\psi_{3d_{\pm2}}\left(\boldsymbol{r}\right) = \Psi_{3,2,\pm2}\left(\boldsymbol{r}\right) = \sqrt{\frac{Z^3}{2\cdot3^4\,\pi}} \cdot (Zr)^2\,e^{-Zr/3}Y_1^{\pm1}\left(\theta,\phi\right)$$

$$= \sqrt{\frac{Z^3}{4\cdot3^8\,\pi}} \cdot (Zr)^2\,e^{-Zr/3}\sin^2\left(\theta\right)e^{\pm 2i\phi}$$

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We define

$$\left\langle \psi_{2s}\left(\boldsymbol{r}\right)|x|\psi_{2p_{\pm1}}\left(\boldsymbol{r}\right)\right\rangle = V_{2s,2p_{\pm1}} \tag{19}$$

and similarly for the other orbitals. Then:

$$V_{2s,2s} = V_{2p_{+1},2p_{-1}} = V_{2p_{\pm1},2p_{\pm1}} = 0 \tag{20}$$

$$V_{2s,2p_{\pm1}} = -\frac{3}{\sqrt{2}} \tag{.21}$$