Chemistry 120A Midterm 2 Solutions
(by Jon Weisberg and Alison Altman)

1. Circle those of the following that are true about the 1-electron atom. Ignore the spin of the individual electron in this problem.

   (a) The binding energy of an electron in any ψ_{nlm} increases as Z^2.
       True

   (b) The radial distribution function of the ψ_{310} eigenstate contains two nodes.
       False

   (c) The ψ_{200} eigenstate can be described by a vibrationally excited state of the bare (l=0) coulomb potential.
       True

   (d) The square of the total orbital angular momentum of an electron in ψ_{322} is larger than the square of its z-component by $2\hbar^2$.
       True

   (e) For an electron in any ψ_{nlm}, the energy, magnitude of angular momentum, and angular momentum in the z-direction are conserved.
       True

   (f) A magnetic field applied in the z-direction would lower the energy of an electron in ψ_{311}.
       False

2. Circle those of the following that are true for a two-electron He atom, including coulomb repulsion between the electrons and spin.

   (a) The spatial wave function of the ground state is described by $\Psi = \psi_{100}(r_1, \theta_1, \phi_1) \times \psi_{100}(r_2, \theta_2, \phi_2)$ with an effective Z less than 2.
       True

   (b) The total binding energy of two electrons in the ground state is larger than $8E_0$.
       False

   (c) The spatial wave function of an excited state of Helium can be described by $\Psi = \psi_{100}(r_1, \theta_1, \phi_1) \times \psi_{210}(r_2, \theta_2, \phi_2)$.
       False

   (d) The ionization energy of pulling an electron out of the $1s2p$ configuration involving single electron orbitals ψ_{100} and ψ_{210} is close to $E_0/4$.
       True

   (e) This is a legitimate slater determinant of two electrons in the ground state, where α denotes spin up and β denotes spin down.

$$\begin{vmatrix} \psi_{100}\alpha(1) & \psi_{100}\alpha(1) \\ \psi_{100}\alpha(2) & \psi_{100}\alpha(2) \end{vmatrix}$$

False

(f) The lowest energy state with a $1s2s$ configuration involving single electron orbitals ψ_{100} and ψ_{200} is a spin triplet.
True

3. (a) The first order energy correction is given by:

$$\langle \phi_0 | V | \phi_0 \rangle = \frac{-\epsilon}{2\pi} \int_0^{2\pi} e^{-i0\theta}(e^{2i\theta} + e^{-2i\theta} - 2)e^{i0\theta} d\theta$$

$$= \frac{-\epsilon}{2\pi} \int_0^{2\pi} e^{2i\theta} + e^{-2i\theta} - 2)d\theta$$

$$= \frac{-\epsilon}{2\pi}[1/2ie^{2i\theta} - 1/2ie^{-2i\theta} - 2]|_0^{2\pi}$$

$$= \frac{-\epsilon}{2\pi}[1/2i(1-1) - 1/2i(1-1) - 2\pi]$$

$$= \frac{-\epsilon}{2\pi}[-2\pi]$$

$$= 2\epsilon$$

(b) The first thing we need to do is construct a matrix of the unperturbed matrix for the $m = \pm 1$, which is given by:

$$\begin{pmatrix} E_1 & 0 \\ 0 & E_1 \end{pmatrix}$$

Where $E_1 = (\hbar^2/2I)$. Next, we must create a perturbation matrix and evaluate each component:

$$\langle \phi_1 | V | \phi_1 \rangle = \frac{-\epsilon}{2\pi} \int_0^{2\pi} e^{-i\theta}(e^{2i\theta} + e^{-2i\theta} - 2)e^{i\theta} d\theta$$

$$= \frac{-\epsilon}{2\pi} \int_0^{2\pi} e^{2i\theta - i\theta + i\theta} + e^{-2i\theta - i\theta + i\theta} - 2e^{-i\theta + i\theta} d\theta$$

$$= \frac{-\epsilon}{2\pi} \int_0^{2\pi} e^{2i\theta} + e^{-2i\theta} - 2e^0 d\theta$$

$$= \frac{-\epsilon}{2\pi}[1/2ie^{2i\theta} - 1/2ie^{-2i\theta} - 2]|_0^{2\pi}$$

$$= \frac{-\epsilon}{2\pi}[1/2i(1-1) - 1/2i(1-1) - 2\pi]$$

$$= \frac{-\epsilon}{2\pi}[-2\pi]$$

$$= 2\epsilon$$

Similarly, $\langle \phi_1 | V | \phi_1 \rangle = 2\epsilon$. The off-diagonal elements are equal and given by:

$$\langle \phi_{-1} | V | \phi_1 \rangle = \frac{-\epsilon}{2\pi} \int_0^{2\pi} e^{i\theta} (e^{2i\theta} + e^{-2i\theta} - 2) e^{i\theta} d\theta$$

$$= \frac{-\epsilon}{2\pi} \int_0^{2\pi} e^{2i\theta + i\theta + i\theta} + e^{-2i\theta + i\theta + i\theta} - 2e^{+i\theta + i\theta} d\theta$$

$$= \frac{-\epsilon}{2\pi} \int_0^{2\pi} e^{4i\theta} + e^0 - 2e^{2i\theta} d\theta$$

$$= \frac{-\epsilon}{2\pi} [1/4i e^{4i\theta} + 1 - 1/i e^{-2i\theta} - 2] |_0^{2\pi}$$

$$= \frac{-\epsilon}{2\pi} [1/2i(1-1) + 2\pi - 1/i(1-1)i]$$

$$= \frac{-\epsilon}{2\pi} [2\pi]$$

$$= -\epsilon$$

Therefore, your perturbation matrix is given by:

$$\begin{pmatrix} 2\epsilon & -\epsilon \\ -\epsilon & 2\epsilon \end{pmatrix}$$

And the total hamiltonian matrix is given by:

$$\begin{pmatrix} E_1 + 2\epsilon & -\epsilon \\ -\epsilon & E_1 + 2\epsilon \end{pmatrix}$$

To find the energies of this system, we must diagonalize the matrix by finding when the determinate of the following matrix is 0:

$$\begin{vmatrix} E_1 + 2\epsilon - E & -\epsilon \\ -\epsilon & E_1 + 2\epsilon - E \end{vmatrix}$$

This gives:

$$(E_1 + 2\epsilon - E)^2 - \epsilon^2 = 0$$
$$(E_1 + 2\epsilon - E)^2 = \epsilon^2$$
$$E_1 + 2\epsilon - E = \pm \epsilon$$
$$E_1 + 2\epsilon \pm \epsilon = E_\pm$$

Therefore, $E_+ = E_1 + 3\epsilon$ and $E_- = E_1 + \epsilon$.

(c) To find the two new wave functions, we need to plug in our new solutions to:

$$\begin{bmatrix} E_1 + 2\epsilon - E & -\epsilon \\ -\epsilon & E_1 + 2\epsilon - E \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = 0$$

E_- (the lower energy solution) gives:

$$\begin{bmatrix} \epsilon & -\epsilon \\ -\epsilon & \epsilon \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = 0$$

When we multiply these matrices, we find that $a_1 = a_2$ or $\Psi_- = 1/\sqrt{2}(|\psi_1\rangle + |\psi_{-1}\rangle)$. Similarly, E_+ (the higher energy solution) gives:

$$\begin{bmatrix} -\epsilon & -\epsilon \\ -\epsilon & -\epsilon \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = 0$$

Here we find that $a_1 = -a_2$ or $\Psi_+ = 1/\sqrt{2}(|\psi_1\rangle - |\psi_{-1}\rangle)$.

(d) $\Psi_+ = 1/\sqrt{2}(|\psi_1\rangle - |\psi_{-1}\rangle)$. We plug and then we chug...

$$\langle V \rangle = \frac{-\epsilon}{2 * 2\pi} \int_0^{2\pi} (e^{-i\phi} - e^{i\phi})(e^{i2\phi} + e^{-i2\phi} - 2)(e^{-i\phi} - e^{i\phi})$$

$$= \frac{-\epsilon}{2 * 2\pi} \int_0^{2\pi} (2 - e^{-2i\phi} - e^{2i\phi})(e^{i2\phi} + e^{-i2\phi} - 2)$$

$$= \frac{-\epsilon}{2 * 2\pi} \int_0^{2\pi} (2 - e^{-2i\phi} - e^{2i\phi})(e^{i2\phi} + e^{-i2\phi} - 2)$$

$$= \frac{-\epsilon}{2 * 2\pi} \int_0^{2\pi} (2e^{2i\phi} + 2e^{-2i\phi} - 4 - e^{i4\phi} - 1 - 2e^{i2\phi} - 1 - e^{-i4\phi} + 2e^{-i2\phi})$$

$$= \frac{-\epsilon}{2 * 2\pi} \int_0^{2\pi} (-6 + 2e^{2i\phi} + 2e^{-2i\phi} - e^{i4\phi} - 2e^{i2\phi} - e^{-i4\phi} + 2e^{-i2\phi})$$

$$= \frac{\epsilon}{2 * 2\pi} 6 * 2\pi = 3\epsilon$$

We integrate over all the $e^{in\phi}$ to get zero. The fact that this energy is the same as the deviation from $E_{1,-1}$ is a result of the 2 state degenerate system. Because the superposition is of 2 eigenstates of the same energy (which is the kinetic energy only), we could equate the total energy to the kinetic plus potential and cancel the kinetic to get this answer. If it was not clear, the new eigenstates can also be written: $\Psi_+ \propto \sin\phi$ and $\Psi_- \propto \cos\phi$. The Ψ_+ wavefunction is higher in energy because there is high electron density in the regions where the potential is high (in energy). This is clear because the density and potential both go as $\sin^2\phi$.

(e) No other states are split. The integral $\langle \phi_{-m}|V|\phi_m\rangle$ can only be nonzero for $m = \pm 1$. Since we already took care of that state above, we conclude that no other states are split.

(f) Any triplet state is acceptable. This means we need a symmetric spin function and and an anti symmetric spatial function. Any of the three spin functions

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$(m_s = -1, 01$) is fine.

$$\Psi = \frac{1}{\sqrt{2}}(\psi_+(1)\psi_-(2) - \psi_+(2)\psi_-(1))[\alpha(1)\alpha(2)]$$
$$\propto (\sin(\phi_1)\cos(\phi_2) - \sin(\phi_2)\cos(\phi_1)[\alpha(1)\alpha(2)]$$
$$\propto (e^{-i\phi_1}e^{i\phi_2} - e^{-i\phi_2}e^{i\phi_1})[\alpha(1)\alpha(2)]$$

Or some similar form based on which order you want to write it in. The difference in order would acrue a minus sign, and would be lost upon squaring for densities.