Chemistry 120A, Spring 2009

Midterm 2 Solutions

March 20, 2009

Problems

Problem 1: Multiple choice problems: 7×3 = 21 points

1. Linear combination of solutions to the time-dependent Schrödinger equation are solutions of the time-dependent Schrödinger equation:

   (a) always (b) sometimes (c) never **A**

2. Linear combination of solutions to the time-independent Schrödinger equation are solutions of the time-independent Schrödinger equation.

   (a) always (b) sometimes (c) never **B**

3. As the force constant k associated witha diatomic molecule is increased, the uncertainty in the momentum in the vibrational ground state will:

   (a) increase (b) decrease (c) stay the same **A**

4. How do you expect the wavelength of the $n = 1$ to $n = 2$ transition in the H atom to compare with the same transition in the He^+ atom?

   (a) longer in H (b) longer in He^+ (c) same **A**

5. Is it possible to simultaneously know the total value of angular momentum and its component along the x axis?

   (a) always (b) sometimes (c) never **A**

6. In the linear variational method, can an approximated ground state energy be below the true ground state energy?

   (a) always (b) sometimes (c) never **C**

7. What is the symmetry of this spin wavefunction with respect to particle interchange?

$$\Psi(1,2) = \alpha(1)\beta(2) - \alpha(1)\beta(2)$$

   (a) symmetric (b) antisymmetric (c) neither **B**

Problem 2 (20 Points): Perturbartion theroy: You know the soltuions to the problem:

$$\hat{H}^{(0)} \left|\psi_m^{(0)}\right\rangle = E_m^{(0)} \left|\psi_m^{(0)}\right\rangle$$

and you are going to try to solve for the eigenvalues and eigenvectors of a related problem:

$$\hat{H} \left|\psi_m^{(0)}\right\rangle = E_m \left|\psi_m^{(0)}\right\rangle$$

where the difference between the two problems is called the perturbation:

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{V}^{(1)}$$

and the strength of the perturbation is measured by some parameter λ.

(a) (8 points) By writing power series expanstions in λ for the eigenvalues and eigenvectors, derive an expression for the leading correction to the eigenvalues of the solved problem due to the presence of the perturbation.

The power series expations in λ for the eigenvalues and eigenfunctions is given by:

$$\begin{aligned} E_0 &= E_0^{(0)} + \lambda E_0^{(1)} + \lambda^2 E_0^{(2)} + \ldots \\ |\psi\rangle &= \left|\psi^{(0)}\right\rangle + \lambda \left|\psi^{(1)}\right\rangle + \lambda^2 \left|\psi^{(2)}\right\rangle + \ldots \end{aligned}$$

We can write the Schrödinger equation, using the Hamiltonian $\left(\hat{H} = \hat{H}^{(0)} + \lambda \hat{V}^{(1)}\right)$. Since we are solving for the leading expression, we only need the terms which have λ to the first power.

$$\begin{aligned} \hat{H} |\psi\rangle &= E |\psi\rangle \\ \left(\hat{H}^{(0)} + \lambda \hat{V}^{(1)}\right)\left(\left|\psi^{(0)}\right\rangle + \lambda \left|\psi^{(1)}\right\rangle + \ldots\right) &= \left(E_0^{(0)} + \lambda E_0^{(1)} + \ldots\right)\left(\left|\psi^{(0)}\right\rangle + \lambda \left|\psi^{(1)}\right\rangle + \ldots\right) \\ \lambda \hat{H}^{(0)} \left|\psi^{(1)}\right\rangle + \lambda V^{(1)} \left|\psi^{(0)}\right\rangle &= \lambda E^{(0)} \left|\psi^{(1)}\right\rangle + \lambda E^{(1)} \left|\psi^{(0)}\right\rangle \\ \hat{H}^{(0)} \left|\psi^{(1)}\right\rangle + V^{(1)} \left|\psi^{(0)}\right\rangle &= E^{(0)} \left|\psi^{(1)}\right\rangle + E^{(1)} \left|\psi^{(0)}\right\rangle \\ \text{Left project with } \left\langle\psi^{(0)}\right| & \\ \left\langle\psi^{(0)}\right| \hat{H}^{(0)} \left|\psi^{(1)}\right\rangle + \left\langle\psi^{(0)}\right| V^{(1)} \left|\psi^{(0)}\right\rangle &= \left\langle\psi^{(0)}\right| E^{(0)} \left|\psi^{(1)}\right\rangle + \left\langle\psi^{(0)}\right| E^{(1)} \left|\psi^{(0)}\right\rangle \\ E^{(1)} \left\langle\psi^{(0)}\middle|\psi^{(1)}\right\rangle + \left\langle\psi^{(0)}\middle|\hat{V^{(1)}}\middle|\psi^{(0)}\right\rangle &= E^{(1)} \left\langle\psi^{(0)}\middle|\psi^{(0)}\right\rangle + E^{(0)} \left\langle\psi^{(0)}\middle|\psi^{(1)}\right\rangle \\ E^{(1)}(0) + \left\langle\psi^{(0)}\middle|\hat{V^{(1)}}\middle|\psi^{(0)}\right\rangle &= E^{(1)}(1) + E^{(0)}(0) \\ E^{(1)} &= \left\langle\psi^{(0)}\middle|\hat{V^{(1)}}\middle|\psi^{(0)}\right\rangle \end{aligned}$$

(b) (7 points) Suppose the know problem you begin with is a three-leve system for which the unperturbed Hamiltonian and the perturbation are given by the matrices below:

$$\mathbf{H}^{(0)} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 4 \end{bmatrix}, \quad \lambda\mathbf{V}^{(1)} = \begin{bmatrix} 0 & -2 & -1 \\ -2 & 1 & 1 \\ -1 & 1 & -1 \end{bmatrix}$$

Evaluate the first order correction to the first excited state.

The basis for $\mathbf{H}^{(0)}$ is given by

$$|1\rangle = \begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} \quad |2\rangle = \begin{bmatrix} 0 \\ 1 \\ 0 \end{bmatrix} \quad |3\rangle = \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix}$$

Therefore, the $\mathbf{V}^1$ matrix is given by

$$\mathbf{V}^{(1)} = \begin{bmatrix} \left\langle 1\middle|\hat{V^{(1)}}\middle|1\right\rangle & \left\langle 1\middle|\hat{V^{(1)}}\middle|2\right\rangle & \left\langle 1\middle|\hat{V^{(1)}}\middle|3\right\rangle \\ \left\langle 2\middle|\hat{V^{(1)}}\middle|1\right\rangle & \left\langle 2\middle|\hat{V^{(1)}}\middle|2\right\rangle & \left\langle 2\middle|\hat{V^{(1)}}\middle|3\right\rangle \\ \left\langle 3\middle|\hat{V^{(1)}}\middle|1\right\rangle & \left\langle 3\middle|\hat{V^{(1)}}\middle|2\right\rangle & \left\langle 3\middle|\hat{V^{(1)}}\middle|3\right\rangle \end{bmatrix} = \begin{bmatrix} 0 & -2 & -1 \\ -2 & 1 & 1 \\ -1 & 1 & -1 \end{bmatrix}$$

The first order corrections are given by the diagonal elements. The first order correction to the ground state is:

$$E_0^{(1)} = \left\langle 1\middle|\hat{V^{(1)}}\middle|1\right\rangle = 0$$

The first order correction to the first excited state is:

$$E_1^{(1)} = \left\langle 2\middle|\hat{V^{(1)}}\middle|2\right\rangle = 1$$

(c) (5 points) Explain whether you expect your answers from part (b) to be accurate or inaccurate, in a concise sentence or two.

It is inaccurate, because $\mathbf{V}^{(1)}$ is the same order of magnitude as $\mathbf{H}^{(0)}$. Perturbation theory only works when the perturbation is small with repect to the unperturbed Hamiltonian. Therefore, many orders are needed to accurately describe the perturbed system.

Problem 3 (18 points) Variational method.

(a) (10 points) Explain clearly what the linear variational method is, usingas an example a problem with two orthonormal trial functions. Your explanation should include a description of how an approximate energy should be calculated.

In the variational method, a guess wavefunction, $\left|\widetilde{\psi}\right\rangle$, is chosen as an approximation to an exact wavefunction which is unknown. The guess wavefunction generally contains variables that can be optimized to yield the lowest approximated energy,

$$\widetilde{E} = \frac{\left\langle \widetilde{\psi}\middle|\hat{H}\middle|\widetilde{\psi}\right\rangle}{\left\langle \widetilde{\psi}\middle|\widetilde{\psi}\right\rangle}$$

The variational theorem states that the approximate energy $\widetilde{E}$ can never be lower that the exact ground state energy, E_0.
In the linear variational method, the guess wavefunction is a linear combination of functions: $\left|\widetilde{\psi}\right\rangle = \sum_j |\phi_j\rangle\, c_j$, where the c_j's are the variatonal parameters. If we minimize the energy $\widetilde{E}$ with resepct to each c_j, the problem becomes a generalized eigenvalue problem: $\mathbf{Hc} = \widetilde{E}\mathbf{Sc}$, where $H_{\alpha\beta} = \left\langle \phi_\alpha\middle|\hat{H}\middle|\phi_\beta\right\rangle$ and $S_{\alpha\beta} = \langle\phi_\alpha|\phi_\beta\rangle$.
In this problem, we are given two orthonormal trial functions, so the overlap matrix is given by:

$$\mathbf{S} = \begin{bmatrix} \langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle \\ \langle\phi_2|\phi_1\rangle & \langle\phi_2|\phi_2\rangle \end{bmatrix} = \begin{bmatrix} 1 & 0 \\ 0 & 1 \end{bmatrix}$$

Which is the identity matrix. Therefore, the generalized eigenvalue problem simplifies to one we know how to solve: $\mathbf{Hc} = \widetilde{E}\mathbf{c}$. The approximate energies are the eigenvalues $\left(\widetilde{E}\right)$ of $\mathbf{H}$.

(b) (8 points) Solve the problem given in question 2(b) by the variational method, using as trial functions the ground state and first excited state of the unperturbed system. Show all of your working clearly, and obtain the approximate energy of the ground state of the system described by $\mathbf{H}$.

From 2(b), we have:

$$\mathbf{H} = \mathbf{H}^{(0)} + \lambda\mathbf{V}^{(1)}$$

But since we are using only the ground state and the first excited state as our trial functions, we only take the 1^{st} quadrant of the full matricies.

$$\mathbf{H} = \begin{bmatrix} 1 & 0 \\ 0 & 2 \end{bmatrix} + \begin{bmatrix} 0 & -2 \\ -2 & 1 \end{bmatrix} = \begin{bmatrix} 1 & -2 \\ -2 & 3 \end{bmatrix}$$

Now, we need to find the eigenvalues of this matrix.

$$|\mathbf{H} - \lambda\mathbf{I}| = 0$$

$$\begin{vmatrix} 1-\lambda & -2 \\ -2 & 3-\lambda \end{vmatrix} = 0$$
$$(1-\lambda)(3-\lambda) - 4 = 0$$
$$3 - \lambda - 3\lambda + \lambda^2 - 4 = 0$$
$$\lambda^2 - 4\lambda - 1 = 0$$
$$\lambda = \frac{4 \pm \sqrt{16+4}}{2}$$
$$\lambda = \frac{4 \pm \sqrt{20}}{2}$$
$$\lambda = 2 \pm \sqrt{5}$$

The lowest energy wil lbe the ground state energy, therefore we have $E_0 = 2 - \sqrt{5} \approx -0.236$.

Problem 4 (16 points) Angular momentum algebra.

(a) (8 points) Classically, angular momentum is a vector, $\mathbf{L} = \mathbf{r} \times \mathbf{p}$. Derive a differential expression for the quantum operator describing the y component of angular momentum from the operators for position and momentum.

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} = \begin{vmatrix} i & j & k \\ r_x & r_y & r_z \\ p_x & p_y & p_z \end{vmatrix}$$

We know that the operators for position and momentum are given by:

$$\hat{r}_x = x \qquad \hat{r}_y = y \qquad r_z = z$$
$$\hat{p}_x = \frac{\hbar}{i}\frac{\partial}{\partial x} \quad \hat{p}_y = \frac{\hbar}{i}\frac{\partial}{\partial y} \quad \hat{p}_z = \frac{\hbar}{i}\frac{\partial}{\partial z}$$

Therefore,

$$\hat{L} = \hat{r} \times \hat{p} = \begin{vmatrix} i & j & k \\ \hat{r}_x & \hat{r}_y & \hat{r}_z \\ \hat{p}_x & \hat{p}_y & \hat{p}_z \end{vmatrix} = \begin{vmatrix} i & j & k \\ x & y & z \\ \frac{\hbar}{i}\frac{\partial}{\partial x} & \frac{\hbar}{i}\frac{\partial}{\partial y} & \frac{\hbar}{i}\frac{\partial}{\partial z} \end{vmatrix}$$

To find the y component of the angular momentum, we evaluate the following determinant:

$$\begin{aligned} \hat{L}_y &= -\begin{vmatrix} x & z \\ \frac{\hbar}{i}\frac{\partial}{\partial x} & \frac{\hbar}{i}\frac{\partial}{\partial z} \end{vmatrix} \\ &= -\left(x\frac{\hbar}{i}\frac{\partial}{\partial z} - z\frac{\hbar}{i}\frac{\partial}{\partial x} \right) \\ &= \frac{\hbar}{i}\left(-x\frac{\partial}{\partial z} + z\frac{\partial}{\partial x} \right) \end{aligned}$$

(b) (8 points) Using the fact that the components of angular momentum have the following commutation relationship that can be summarized as $\mathbf{L} \times \mathbf{L} = i\hbar\mathbf{L}$, evaluate the following commutator: $\left[\hat{L_x^2}, \hat{L_z}\right]$.

First, we know from $\mathbf{L} \times \mathbf{L} = i\hbar\mathbf{L}$ (remembering $\mathbf{L}$ is a vector) that

$$\left[\hat{L_x}, \hat{L_z}\right] = -i\hbar\hat{L}_y$$

Therefore, $\hat{L}_x$ and $\hat{L}_z$ do not commute. This means we must preserve the order of the operators throughout this problem.

$$\begin{aligned}
\left[\hat{L_x^2}, \hat{L_z}\right] &= \hat{L}_x^2\hat{L}_z - \hat{L}_z\hat{L}_x^2 \\
&= \hat{L}_x\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x\hat{L}_x \\
&= \hat{L}_x\hat{L}_x\hat{L}_z - \hat{L}_x\hat{L}_z\hat{L}_x + \hat{L}_x\hat{L}_z\hat{L}_x - \hat{L}_z\hat{L}_x\hat{L}_x \\
&= \hat{L}_x\left(\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x\right) + \left(\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x\right)\hat{L}_x \\
&= \hat{L}_x\left[\hat{L_x}, \hat{L_z}\right] + \left[\hat{L_x}, \hat{L_z}\right]\hat{L}_x \\
&= \hat{L}_x\left(-i\hbar\hat{L}_y\right) + \left(-i\hbar\hat{L}_y\right)\hat{L}_x \\
&= -i\hbar\hat{L}_x\hat{L}_y - i\hbar\hat{L}_y\hat{L}_x \\
&= -i\hbar\left(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x\right)
\end{aligned}$$

A second way of doing this starts with the commutator definition:

$$\begin{aligned}
\left[\hat{L_x}, \hat{L_z}\right] &= -i\hbar\hat{L}_y \\
\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x &= -i\hbar\hat{L}_y
\end{aligned}$$

Which we can use to obtain the following two relations:

$$\begin{aligned}
\hat{L}_x\hat{L}_z &= \hat{L}_z\hat{L}_x - i\hbar\hat{L}_y \\
\hat{L}_z\hat{L}_x &= \hat{L}_x\hat{L}_z + i\hbar\hat{L}_y
\end{aligned}$$

Now, moving to the commutator of $\hat{L}_x^2$ and $\hat{L}_z$:

$$\begin{aligned}
\left[\hat{L_x^2}, \hat{L_z}\right] &= \hat{L}_x^2\hat{L}_z - \hat{L}_z\hat{L}_x^2 \\
&= \hat{L}_x\hat{L}_x\hat{L}_z - \hat{L}_z\hat{L}_x\hat{L}_x \\
&= \hat{L}_x\left(\hat{L}_x\hat{L}_z\right) - \left(\hat{L}_z\hat{L}_x\right)\hat{L}_x \\
&= \hat{L}_x\left(\hat{L}_z\hat{L}_x - i\hbar\hat{L}_y\right) - \left(\hat{L}_x\hat{L}_z + i\hbar\hat{L}_y\right)\hat{L}_x \\
&= \hat{L}_x\hat{L}_z\hat{L}_x - i\hbar\hat{L}_x\hat{L}_y - \hat{L}_x\hat{L}_z\hat{L}_x - i\hbar\hat{L}_y\hat{L}_x \\
&= -i\hbar\hat{L}_x\hat{L}_y - i\hbar\hat{L}_y\hat{L}_x \\
&= -i\hbar\left(\hat{L}_x\hat{L}_y + \hat{L}_y\hat{L}_x\right)
\end{aligned}$$