CHEMISTRY 542

ANSWERS to Exam III

November 22, 2004

In applying the principles of Quantum Mechanics in answering each question, be sure to *state the principle you are using at each step*.

1. Given the complete orthonormal set of functions { φ_1 , φ_2 , φ_3 , φ_4 } which are eigenfunctions of operator $\mathcal{F}$ with eigenvalues $(3/2)\hbar$, $½\hbar$, $-½\hbar$, $-(3/2)\hbar$ respectively. The operator $\mathcal{B}$ has this relation to $\mathcal{F}$: $[\mathcal{B}, \mathcal{F}] = 0$, and G is a function.
(a) Determine the results of the following, where possible; otherwise say "more information needed":

	Answer	Principles
$\int\varphi_1{}^*\varphi_1 d\tau$	1	(Given) the functions are normalized
$\int\varphi_1{}^*\varphi_3 d\tau$	0	(Given) the eigenfunctions of a Hermitian operator form a complete orthonormal set. Eigenfunctions of an operator that correspond to different eigenvalues are necessarily orthogonal to each other
$\int\varphi_2{}^*\mathcal{F}\varphi_2 d\tau$	$½\hbar$	Postulate 2: $\mathcal{F}\varphi_2 = ½\hbar\varphi_2$, and (given) φ_2 is one of the eigenfunctions of $\mathcal{F}$ with eigenvalue $½\hbar$
$\int\varphi_1{}^*\mathcal{F}\varphi_3 d\tau$	0	Postulate 2, and (given) φ_3 is one of the eigenfunctions of $\mathcal{F}$, and eigenfunctions of an operator that correspond to different eigenvalues are necessarily orthogonal to each other.
$\int\varphi_1{}^*\mathcal{B}\varphi_4 d\tau$	0	commuting Hermitian operators have simultaneous set of eigenfunctions, with one-to-one correspondence when non-degenerate, and the eigenfunctions of a Hermitian operator form a complete orthonormal set
$\int\varphi_1{}^*\mathcal{F}^3\varphi_1 d\tau$	$[(3/2)\hbar]^3$	Postulate 2: $\mathcal{F}\varphi_1 = ½\hbar\varphi_1$, and (given) φ_1 is one of the eigenfunctions of $\mathcal{F}$ with eigenvalue $(3/2)\hbar$
$\int\varphi_4{}^*\{\mathcal{F}^2 - [(3/2)\hbar]^2\}G d\tau$	0 (for any G)	Definition of a Hermitian operator $\mathcal{F}$, and (given) φ_4 is one of the eigenfunctions of $\mathcal{F}$ with eigenvalue $-(3/2)\hbar$
$\int\varphi_1{}^*\mathcal{B}^2\mathcal{F}\varphi_3 d\tau$	0	Postulate 2: $\mathcal{F}\varphi_3 = -½\hbar\varphi_3$, and (given) φ_3 is one of the eigenfunctions of $\mathcal{F}$ and that commuting Hermitian operators have simultaneous set of eigenfunctions, with one-to-one correspondence when non-degenerate

(b) Suppose the system is in a state $\Psi = 2^{-½}\varphi_1 + 3^{-½}\varphi_3 + 6^{-½}\varphi_4$
When the property F is measured for the system, what values would result with what probability?

The eigenvalues $(3/2)\hbar$, $-½\hbar$, $-(3/2)\hbar$ only, respectively, with probability ½, 1/3 and 1/6.
[resulting in an average = $½(3/2)\hbar + (-½\hbar)/3 + -(3/2)\hbar/6 = \hbar/3$ (not required)]

(c) What is the matrix representation of $\mathcal{F}$ in the basis set { φ_1 , φ_2 , φ_3 , φ_4 }?

$$\mathcal{F} = \begin{array}{cccc} \varphi_1 & \varphi_2 & \varphi_3 & \varphi_4 \\ (3/2)\hbar & 0 & 0 & 0 \\ 0 & ½\hbar & 0 & 0 \\ 0 & 0 & -½\hbar & 0 \\ 0 & 0 & 0 & -(3/2)\hbar \end{array}$$

2. Consider a Li atom.

(a) Write the time-independent non-relativistic Schrödinger equation for the Li atom.

After separating out translation (center-of-mass coordinates) the electronic motion is described by

$$\left[-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2+\nabla_3^2\right)-3e^2\left(\frac{1}{r_1}+\frac{1}{r_2}+\frac{1}{r_3}\right)+e^2\left[\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{23}}\right]\right]\Psi(1,2,3)=E\,\Psi(1,2,3)$$

where ∇_i^2 is in terms of x_i, y_i, z_i coordinates of electron i relative to the nucleus.

(b) Neglecting both electron-electron repulsion and electron spin, consider the form of the wavefunctions of the Li atom which satisfy the above equation. Write the total wavefunction, including all the parts as explicitly as you can. Briefly explain how you arrived at this answer.

Neglecting e-repulsion leaves out $e^2\left(\frac{1}{r_{12}}+\frac{1}{r_{13}}+\frac{1}{r_{23}}\right)$ and neglecting spin leaves out antisymmetrization (Pauli principle) requirement. Besides the translational function as a factor we have

$$\Psi(\vec{r}_1,\vec{r}_2,\vec{r}_3)=R_{n_1l_1}(r_1)\cdot Y_{l_1m_1}(\theta_1,\phi_1)\cdot R_{n_2l_2}(r_2)\cdot Y_{l_2m_2}(\theta_2,\phi_2)\times\cdot R_{n_3l_3}(r_3)\cdot Y_{l_3m_3}(\theta_3,\phi_3)$$

where $R_{n_il_i}(r_i)$ are the exact radial functions of the H atom with $Z=3$ and $Y_{l_im_i}(\theta_i,\phi_i)$ are the exact spherical harmonic functions as for the H atom with the same quantum numbers

The translational function looks like for a box A×B×C:

$$\psi_{transl}(X_{cm},Y_{cm},Z_{cm})=\sqrt{\frac{2}{A}}\sin\left(\frac{n_x\pi}{A}X_{cm}\right)\cdot\sqrt{\frac{2}{B}}\sin\left(\frac{n_y\pi}{B}Y_{cm}\right)\times\cdot\sqrt{\frac{2}{C}}\sin\left(\frac{n_z\pi}{C}Z_{cm}\right)$$

(c) Neglecting electron-electron repulsion but taking into account electron spin, and neglecting spin-orbit interaction, consider the form of the wavefunctions of the Li atom. Write out the terms in the total wavefunction, including all the parts as explicitly as you can. Briefly explain how you arrived at this answer.

Taking into account electron spin requires incorporating Pauli exclusion principle, (which the translational wfn, is not involved)

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{r}_3) = \frac{1}{\sqrt{3!}} \det \underbrace{\begin{vmatrix} \psi^{\alpha}_{n_1 l_1 m_1}(1) & \psi^{\beta}_{n_2 l_2 m_2}(1) & \psi^{\alpha}_{n_3 l_3 m_3}(1) \\ \psi^{\alpha}_{n_1 l_1 m_1}(2) & \psi^{\beta}_{n_2 l_2 m_2}(2) & \psi^{\alpha}_{n_3 l_3 m_3}(2) \\ \psi^{\alpha}_{n_1 l_1 m_1}(3) & \psi^{\beta}_{n_2 l_2 m_2}(3) & \psi^{\alpha}_{n_3 l_3 m_3}(3) \end{vmatrix}}_{\text{call this } D}$$

where $\psi_{n_i l_i m_i} = R_{n_i l_i}(r_i) \cdot Y_{l_i m_i}(\theta_i, \phi_i)$ as on previous page.

for the configuration $\psi_{n_1 l_1 m_1}\alpha \cdot \psi_{n_2 l_2 m_2}\beta \cdot \psi_{n_3 l_3 m_3}\alpha(3)$

[For the ground configuration, we have a doublet D_I and D_{II} where D_I is for the config $1s^2 2s\alpha$
D_{II} is for the config $1s^2 2s\beta$]

In general, at this level of theory,
$\psi_{n_1 l_1 m_1}$ are exact hydrogen atom functions with $Z = 3$, as on previous page.

(d) Including electron-electron repulsion by using a central field and Slater's rules, and taking into account electron spin, consider the form of the wavefunctions of the Li atom. Start by writing out the potential energy terms in the time-independent non-relativistic Hamiltonian using Slater's rules.

$$V = -e^2\left(\frac{Z_1}{r_1} + \frac{Z_2}{r_2} + \frac{Z_3}{r_3}\right) \quad \text{where } Z_i = 3 - s_i$$

where s_i depends on the electron configuration. For configuration $1s^2 2s$ for example

$s_1 = 0.30 \quad s_2 = 0.30 \quad s_3 = 0.85$

Now show the time-independent non-relativistic Schrödinger equation for the Li atom that you will have to solve, assuming the translational part has already been separated out. Be as explicit as possible, including variables and quantum numbers where appropriate.

$$\left[-\frac{\hbar^2}{2m}\left(\nabla_1^2+\nabla_2^2+\nabla_3^2\right)-e^2\left(\frac{Z_1}{r_1}+\frac{Z_2}{r_2}+\frac{Z_2}{r_3}\right)\right]\Psi_{n_1l_1m_1}(r_1,\theta_1,\phi_1)\cdot\Psi_{n_2l_2m_2}(r_2,\theta_2,\phi_2)\cdot\Psi_{n_3l_3m_3}(r_3,\theta_3,\phi_3) = E\,\Psi_{n_1l_1m_1}(r_1,\theta_1,\phi_1)\cdot\Psi_{n_2l_2m_2}(r_2\theta_2\phi_2)\cdot\Psi_{n_3l_3m_3}(r_3\theta_3\phi_3)$$

where

$$\Psi_{n_il_im_i}(r_i,\theta_i,\phi_i)=\underbrace{R_{n_il_i}(Z_i,r_i)}\cdot Y_{l_im_i}(\theta_i,\phi_i)$$

in which this part is just like the H-atom functions, except with Z_i according to Slater, and only the leading power of r_i in the radial H atom function (Laguerre polynomial) is included and the r_i function is re-normalized

Write out the terms in the total wavefunction, taking into account electron spin, but neglecting spin-orbit coupling, including all the parts as explicitly as you can.

The answer is the same as in (c) in previous page, except for $\psi_{n_il_im_i}$ we use the functions in the box above.

3. Consider a particle of mass M in a nonstationary state in a one-dimensional box of length a. Suppose that at time t_0, its state function is the parabolic function
$\Psi(t_0) = Nx(a-x) \qquad 0 \leq x \leq a$, where N is the normalization constant.
(a) Expand this non-stationary state function in terms of the energy eigenfunctions of the particle. Calculate the expansion coefficients.

$\Psi = \sum_n c_n \varphi_n$. To find the $m_{\underline{th}}$ coefficient, operate on both sides with $\int_0^a \varphi_m^* dx$
$\int_0^a \varphi_m^* Nx(a-x)\,dx = \int_0^a \varphi_n^* \sum_n c_n \varphi_n\,dx$. Since $\int_0^a \varphi_m^* \varphi_n\,dx = \delta_{mn}$, only c_m survives.
$\int_0^a \varphi_m^* Nx(a-x)\,dx = \int_0^a (2/a)^{1/2} \sin(m\pi x/a)\, Nx(a-x)\,dx = c_m$
$= N(2/a)^{1/2}\{a\int_0^a \sin(m\pi x/a)x\,dx - \int_0^a \sin(m\pi x/a)x^2\,dx\} = N(2/a)^{1/2}\{-2a^3(\cos m\pi-1)/m^3\pi^3\} = c_m$
Therefore, $c_m = 0$ for m = even and $c_m = N(2/a)^{1/2}\,4a^3/m^3\pi^3$ for m = odd.

We need to do normalization integral $\int_0^a N^*x(a-x)Nx(a-x)dx = 1$ to find N.
$N^2 \int_0^a x^2(a-x)^2\,dx = 1$
$N^2 \int_0^a (a^2x^2+x^4-2ax^3)dx = 1$
$N^2\, |{}^1/_3 a^2x^3 + {}^1/_5 x^5 - \tfrac{1}{2}ax^4|_0^a = 1$
$N^2\, a^5/30 = 1$
$N = a^{-5/2}\sqrt{30}$

(b) If at time t_0 we were to make a series of measurements of the particle's energy, what would be the possible outcomes of such measurements?

We would get $n^2h^2/8Ma^2$ where n = 1,3,5,7,9, etc. only odd integer values

(c) What would the average of such measurements be?

$$\langle E\rangle = \frac{\int_0^a N^*x(a-x)\mathcal{H}\,Nx(a-x)dx}{\int_0^a N^*x(a-x)Nx(a-x)dx} = -(\hbar^2/2M)\,\frac{\int_0^a N^*x(a-x)\,(d^2/dx^2)\,Nx(a-x)dx}{\int_0^a N^*x(a-x)\,Nx(a-x)dx}$$

$(d/dx)\,[x(a-x)] = (d/dx)\,[a-2x] = -2$

$$\langle E\rangle = -(\hbar^2/2M)\,\frac{\int_0^a x(a-x)(-2)dx}{\int_0^a x^2(a-x)^2\,dx} = (\hbar^2/M)\,\frac{\int_0^a (ax-x^2)dx}{\int_0^a (a^2x^2+x^4-2ax^3)dx} = (\hbar^2/M)\,\frac{|\tfrac{1}{2}ax^2 - {}^1/_3x^3|_0^a}{|{}^1/_3a^2x^3+{}^1/_5x^5-\tfrac{1}{2}ax^4|_0^a}$$

$\langle E\rangle = (\hbar^2/M)(5/a^2) = (5\hbar^2/Ma^2)$

or

$\langle E\rangle = \int_0^a N^*x(a-x)\mathcal{H}\,Nx(a-x)dx = -(\hbar^2/2M)\int_0^a N^*x(a-x)\,(d^2/dx^2)\,Nx(a-x)dx$

$(d/dx)\,[x(a-x)] = (d/dx)\,[a-2x] = -2$
$\langle E\rangle = -(\hbar^2/2M)N^2\int_0^a x(a-x)(-2)dx = (\hbar^2/M)N^2\int_0^a (ax-x^2)dx = (\hbar^2/M)N^2|\tfrac{1}{2}ax^2 - {}^1/_3x^3|_0^a$
$\langle E\rangle = (\hbar^2/M)N^2(a^3/6)$
using $N^2 = 30/a^5$ from part (a),
$\langle E\rangle = (5\hbar^2/Ma^2)$