CHEMISTRY 542

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
$\int\varphi_1{}^*\varphi_1 d\tau$		
$\int\varphi_1{}^*\varphi_3 d\tau$		
$\int\varphi_2{}^*\mathcal{F}\varphi_2 d\tau$		
$\int\varphi_1{}^*\mathcal{F}\varphi_3 d\tau$		
$\int\varphi_1{}^*\mathcal{B}\varphi_4 d\tau$		
$\int\varphi_1{}^*\mathcal{F}^3\varphi_1 d\tau$		
$\int\varphi_4{}^*\{\mathcal{F}^2 - [(3/2)\hbar]^2\}G d\tau$		
$\int\varphi_1{}^*\mathcal{B}^2\mathcal{F}\varphi_3 d\tau$		

(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?

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

2. Consider a Li atom.

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

(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.

(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.

(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.

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 s possible, including variables and quantum numbers where appropriate.

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.

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

$\Psi(t_0) = Nx(a-x)$ $\quad 0 \le x \le a$, 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.

(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?

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

$\{\pi\}^{-1/2}\,(Z/a)^{3/2}\exp[-Zr/a]$; $\tfrac{1}{4}\{2\pi\}^{-1/2}\,(Z/a)^{5/2}\,r\exp[-Zr/2a]\cos\theta$; $|q|^{-1/4}\sin\{(2/3)|q|^{3/2}+\tfrac{1}{4}\pi\}$

$\{2/L\}^{1/2}\sin(n\pi x/L)$; $\{2\pi\}^{-1/2}\exp[im\phi]$; $\{2\omega M/\hbar\}^{1/4}\exp[-\omega M x^2/2\hbar]$

$\int \sin(ax)dx = -(1/a)\cos(ax)$

$\int \cos(ax)dx = (1/a)\sin(ax)$

$\int \sin^2(ax)dx = \tfrac{1}{2}x - (1/4a)\sin(2ax)$

$\int \cos^2(ax)dx = \tfrac{1}{2}x + (1/4a)\sin(2ax)$

$\int \sin(ax)\sin(bx)dx = [1/2(a-b)]\sin[(a-b)x)] - [1/2(a+b)]\sin[(a+b)x)], \quad a^2 \neq b^2$

$\int \cos(ax)\cos(bx)dx = [1/2(a-b)]\sin[(a-b)x)] + [1/2(a+b)]\sin[(a+b)x)], \quad a^2 \neq b^2$

$\int x\sin(ax)dx = (1/a^2)\sin(ax) - (x/a)\cos(ax)$

$\int x\cos(ax)dx = (1/a^2)\cos(ax) + (x/a)\sin(ax)$

$\int x^2\cos(ax)dx = [(a^2x^2-2)/a^3]\sin(ax) + 2x\cos(ax)/a^2$

$\int x^2\sin(ax)dx = -[(a^2x^2-2)/a^3]\cos(ax) + 2x\sin(ax)/a^2$

$\int x\sin^2(ax)dx = x^2/4 - x\sin(2ax)/4a - \cos(2ax)/8a^2$

$\int x^2\sin^2(ax)dx = x^3/6 - [x^2/4a - 1/8a^3]\sin(2ax) - x\cos(2ax)/4a^2$

$\int x\cos^2(ax)dx = x^2/4 + x\sin(2ax)/4a + \cos(2ax)/8a^2$

$\int x^2\cos^2(ax)dx = x^3/6 + [x^2/4a - 1/8a^3]\sin(2ax) + x\cos(2ax)/4a^2$

$\int x\exp(ax)dx = \exp(ax)\,(ax-1)/a^2$

$\int x\exp(-ax)dx = \exp(-ax)\,(-ax-1)/a^2$

$\int x^2\exp(ax)dx = \exp(ax)\,[x^2/a - 2x/a^2 + 2/a^3]$

$\int x^m\exp(ax)dx = \exp(ax)\sum_{r=0 \text{ to } m}(-1)^r\, m!x^{m-r}/(m-r)!a^{r+1}$

$\int_0^\infty x^n\exp(-ax)dx = n!/a^{n+1} \qquad a>0$, n positive integer

$\int_0^\infty x^2\exp(-ax^2)dx = (1/4a)(\pi/a)^{1/2} \qquad a>0$

$\int_0^\infty x^{2n}\exp(-ax^2)dx = (1\cdot3\cdot5\cdot\ldots\cdot(2n-1)/(2^{n+1}a^n)(\pi/a)^{1/2} \qquad a>0$

$\int_0^\infty x^{2n+1}\exp(-ax^2)dx = n!/2a^{n+1} \qquad a>0$, n positive integer

$\int_0^\infty \exp(-a^2x^2)dx = (1/2a)\,(\pi)^{1/2} \qquad a>0$

$\int_0^\infty \exp(-ax)\cos(bx)dx = a/(a^2+b^2) \qquad a>0$

$\int_0^\infty \exp(-ax)\sin(bx)dx = b/(a^2+b^2) \qquad a>0$

$\int_0^\infty x\exp(-ax)\sin(bx)dx = 2ab/(a^2+b^2)^2 \qquad a>0$

$\int_0^\infty x\exp(-ax)\cos(bx)dx = (a^2-b^2)/(a^2+b^2)^2 \qquad a>0$

$\int_0^\infty \exp(-a^2x^2)\cos(bx)dx = [(\pi)^{1/2}/2a]\cdot\exp[-b^2/4a^2] \qquad ab \neq 0$

Slater's rules:

The effective charge seen by the $i\underline{th}$ electron whose quantum numbers are n ℓ in an atom whose atomic number is Z is given by

$$(Z_{eff})_i = Z - s_{n\ell}$$

Slater provides $s_{n\ell}$ as follows:

1. For i having n ℓ= 1s

    $s_{1s} = 0.30k_{same}$

    where

    k_{same} = number of other electrons in the same 1s shell

2. For i having n > 1 and ℓ = 0 or 1

    $s_{n\ell} = 0.35k_{same} + 0.85k_{in} + 1.00k_{inner}$

    where

    k_{same} = number of other electrons in the same shell as the screened electron of interest

    k_{in} = number of electrons in the shell with principal quantum number n-1

    k_{inner} = number of electrons in the shell with principal quantum number n-2

3. For the $i\underline{th}$ electron having quantum numbers n ℓ = 3d

    $s_{3d} = 0.35k_{3d} + 1.00k_{in}$

    where

    k_{3d} = number of other electrons in the same 3d shell

    k_{in} = number of electrons with $n \leq 3$ and $\ell < 2$

For the purposes of Slater's rules, the "subshells" are taken to be in the order innermost 1s (2s,2p) (3s,3p) 3d (4s,4p) outermost

ADDITIONAL INFORMATION

$a_0 = (\hbar^2/m_e e^2)$ the "Bohr radius", 0.529177×10^{-10} m

$(e^2/2a_0) = 13.6057$ eV one rydberg, a unit of energy = (1/2) hartree

c = frequency•wavelength = 2.997924×10^{10} cm sec^{-1} the speed of light

1 eV = 8065.6 cm^{-1}

$\mathcal{L}^2 = -\hbar^2\{ (1/\sin\theta)(\partial/\partial\theta)\sin\theta\, \partial/\partial\theta + (1/\sin^2\theta)\partial^2/\partial\phi^2\}$

$\mathcal{H} = -(\hbar^2/2M)\{(1/r)\partial^2/\partial r^2\, r\}$

$\quad -(\hbar^2/2Mr^2)\{ (1/\sin\theta)(\partial/\partial\theta)\sin\theta\, \partial/\partial\theta + (1/\sin^2\theta)\partial^2/\partial\phi^2\} + V(r)$