Problem Set 9
On the Hydrogen atom
and Matrix Representation of Operators and Eigenfunctions

On the hydrogen atom:

1. Consider a hydrogen-like atom (ion) of charge Z when the atom (ion) is in its ground state:

$$\Psi_{1s} = \{1/\sqrt{\pi}\}\ \{Z/a_0\}^{3/2} \exp[-Zr/a_0]$$

where a_0 is the Bohr radius, $a_0 = \hbar^2/me^2 = 0.529 \times 10^{-8}$ cm.

(a) Calculate the average distance of the electron from the nucleus for this state. You may leave your answer in terms of the Bohr radius.

(b) Calculate the most probable distance of the electron from the nucleus for this state. You may leave your answer in terms of the Bohr radius.

(c) What are the expected outcomes of the measurement of the z component of the electron's orbital angular momentum for the atom in this state, given that the operator for this component is

$$L_z = (\hbar/i)\partial/\partial\varphi \ ?$$

(d) Calculate the average z component of the electron's orbital angular momentum for this ground state.

(e) Does L_z commute with the hamiltonian for a hydrogen-like atom ? Show whether the z component of the electron's orbital angular momentum in this hydrogen-like atom is a constant of the motion. Given that for this system,

$$H = -(\hbar^2/2m)\nabla^2 - Ze^2/r$$

where $\nabla^2 = \partial^2/\partial r^2 + (2/r)\,\partial/\partial r + \{r^2\sin\theta)^{-1}\partial/\partial\theta(\sin\theta\,\partial/\partial\theta) + \{r^2\sin^2\theta)^{-1}(\partial^2/\partial\phi^2)$

2. A hydrogen-like wavefunction is shown below <u>with r in units of a_0.</u>

$$\Psi(r,\theta,\phi) = (1/81)(2/\pi)^{1/2}\, Z^{3/2}\,(6-Zr)\, Zr\, \exp[-Zr/3] \cos\theta$$

(a) Determine the values of the quantum numbers n, ℓ, m for Ψ by inspection. Give the reason for your answers.

n = $\qquad\qquad$ ℓ = $\qquad\qquad$ m =

(b) Determine the most probable value of r for an electron in the state specified by the $\Psi(r,\theta,\phi)$ given above, when Z = 1.

(c) Generate from $\Psi(r,\theta,\phi)$ given above, another eigenfunction having the same values of n and ℓ but with the magnetic quantum number equal to m+1.

The Laplacian $\nabla^2 = \{\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2\}$ when transformed to spherical coordinates becomes $\nabla^2 = \{(1/r^2)\{\partial/\partial r\,(r^2\partial/\partial r) - L^2\}$

(d) Write down the hamiltonian for a hydrogen-like atom (only the internal motion of the electron relative to the nucleus).

(e) Determine whether it is possible to determine simultaneously the energy of a hydrogen atom and its angular momentum.

3. On the hydrogen atom:

(a) The line intensities in the hydrogen atom spectra are directly proportional to the probability of the transition which corresponds to the change in atomic states. This transition probability is proportional to the square of the integral

$$\int \Psi_{n\ell m}^{*}\, x\, \Psi_{n'\ell'm'}\, d\tau$$

where the initial state has quantum numbers $n\ell m$ and the final state has quantum number $n'\ell'm'$. ***Derive*** the relationships between n and n', ℓ and ℓ' , m and m' that have to be satisfied in order that the integral not be zero, that is, so that the transition be allowed. These are the so-called "selection rules" of atomic spectroscopy. [Hint: $x = r \sin\theta \cos\phi$]

(b) H. C. Urey, F,. G. Brickwedde and G. M. Murphy, Phys. Rev. 40, 464 (1932) reported very faint lines accompanying the Balmer lines of the hydrogen spectrum. They attributed the faint lines to the presence of deuterium in the sample since they appeared at the calculated wavelengths for a hydrogen atom of mass 2 amu. ***Derive the explicit expression*** for this isotope shift (the displacement of the deuterium wavelength from the hydrogen wavelength) for the first Balmer line. Note that the answer is expressed in terms of wavelength (Å).

on Matrix Representation of Operators and Wavefunctions

1. Consider a biradical, placed in a magnetic field **B**. The electron spin part of the Hamiltonian for the system is

$$H_{op} = a_1 S_z(1) + a_2 S_z(2) + J\mathbf{S}(1)\bullet\mathbf{S}(2)$$

where $a_1 = g_1\, \mu_B B/\hbar$ $\quad a_2 = g_2\, \mu_B B/\hbar$ $\quad J$ = coupling constant

The operators are the usual spin angular momentum operators for the two electrons. Given that

$S_z(1)\varphi_1(1) = ½\, \hbar\, \varphi_1(1)$

for electron 1

$S_z(1)\varphi_2(1) = -½\, \hbar\, \varphi_2(1)$

$S_z(2)\varphi_1(2) = ½\, \hbar\, \varphi_1(2)$

for electron 2

$S_z(2)\varphi_2(2) = -½\, \hbar\, \varphi_2(2)$

Starting from the definitions $S_+ \equiv S_x + iS_y$ $S_- \equiv S_x - iS_y$
(the ladder operators)

it is trivial to prove that

$$\mathbf{S}(1)\bullet\mathbf{S}(2) = \{ \tfrac{1}{2}S_+(1)S_-(2) + \tfrac{1}{2} S_-(1)S_+(2) + S_z(1) S_z(2) \}$$

What are the eigenvalues and eigenfunctions of S_z for the biradical ?
Using the eigenfunctions of S_z as a complete set of basis functions, *find the matrix representation of* $\mathbf{S}(1)\bullet\mathbf{S}(2)$, H_{op}, and S^2

for $a_1 = 2/\hbar$, $a_2 = 2/\hbar$, $J = 4/\hbar^2$

Calculate all the eigenvalues and determine all the eigenfunctions of H_{op}
Draw the energy level diagram and label each state of the biradical system.

Note that except for the values of a_1, a_2 , and J, the above problem is identical to the problem described by

$H_{op} = a_1S_z + a_2I_z + A\mathbf{I}\bullet\mathbf{S}$

[where $a_1 = g_e \mu_B B/\hbar$ $a_2 = - g_p \mu_N B/\hbar$ A = electron-nuclear hyperfine coupling constant]

which provides all the answers to the NMR and ESR behavior of a hydrogen atom. A is probably the most accurately measured physical constant :
A = 1 420 405 751.786 ± 0.010 Hz or 21 cm. (21 cm is the wavelength to which radiotelescopes are tuned, listening for extraterrestrial messages, the natural frequency of radiation from a hydrogen atom being an obvious choice of an advanced civilization). The famous 21 cm line emitted by hydrogen atoms in outer space was detected by Ewen and Purcell in 1951 when they stuck a horn-shaped antenna out the window of a Harvard physics lab. This experiment marked the beginning of radioastronomy.

or the problem described by

$H_{op} = a_1I_z(1) + a_2I_z(2) + J_{12}\mathbf{I}(1)\bullet\mathbf{I}(2)$

[where $a_1 = - g_1 (1-\sigma_1)\mu_N B/\hbar$ $a_2 = - g_2 (1-\sigma_2)\mu_N B/\hbar$

σ_1 and σ_2 are the nuclear magnetic shielding constants,

J_{12} = nuclear spin - nuclear spin scalar coupling constant]

which describes the NMR behavior of two spin ½ nuclei, such as H and H, or ^{19}F and H, or ^{31}P and H, or ^{13}C and ^{19}F, etc.) in a randomly tumbling molecule in a magnetic field.

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2. Consider particles 1 and 2. Given the operators I_x, I_y, I_z which have the following properties:

$I_z(1)\alpha(1) = \frac{1}{2}\hbar\,\alpha(1)$ $\qquad$ $I_z(1)\,\beta(1) = -\frac{1}{2}\hbar\,\beta(1)$

$I_x(1)\alpha(1) = \frac{1}{2}\hbar\,\beta(1)$ $\qquad$ $I_x(1)\,\beta(1) = \frac{1}{2}\hbar\,\alpha(1)$

$I_y(1)\alpha(1) = \frac{1}{2} i\hbar\,\beta(1)$ $\qquad$ $I_y(1)\,\beta(1) = -\frac{1}{2} i\hbar\,\alpha(1)$

$\alpha(1)$ and $\beta(1)$ are functions associated with particle 1.

$\mathbf{I}(1) \equiv I_x(1)\,\mathbf{i} + I_y(1)\,\mathbf{j} + I_z(1)\,\mathbf{k}$ $\qquad$ **i**, **j**, and **k** are unit vectors along the x, y, and z directions.

Find the simultaneous eigenfunctions of the operators

$F_z \equiv I_z(1) + I_z(2)$ and $F^2 \equiv F_x^2 + F_y^2 + F_z^2$