

## Homework No. 08 (Fall 2013)

### PHYS 530B: Quantum Mechanics II

Due date: Friday, 2013 Nov 22, 4.30pm

1. The Hamiltonian for an hydrogenic atom is

$$H = \frac{p^2}{2\mu} - \frac{Ze^2}{r}. \quad (1)$$

- (a) Using

$$\mathbf{p} = \frac{\hbar}{i} \nabla \quad \text{and} \quad H = -\frac{\hbar}{i} \frac{\partial}{\partial t} \quad (2)$$

in conjunction with the fact that Hamiltonian is a constant of motion, construct the ‘time-independent Schrödinger equation’ for hydrogenic wavefunctions to be

$$\left( -\frac{\hbar^2}{2\mu} \nabla^2 - \frac{Ze^2}{r} \right) \psi_n(\mathbf{r}) = E_n \psi_n(\mathbf{r}). \quad (3)$$

- (b) We shall confine our discussion to bound states ( $E_n < 0$ ). Define

$$E_n = -\frac{\mu Z^2 e^4}{2\hbar^2} \frac{1}{n^2} \quad \text{and} \quad a_0 = \frac{\hbar^2}{\mu e^2}, \quad (4)$$

later being the (first) Bohr radius. Thus, derive

$$\left( \nabla^2 + \frac{2Z}{a_0 r} \right) \psi_n(\mathbf{r}) = \frac{Z^2}{a_0^2} \frac{1}{n^2} \psi_n(\mathbf{r}). \quad (5)$$

- (c) The Laplacian in spherical polar coordinates is

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{1}{r^2} \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right). \quad (6)$$

Since angular momentum is a constant of motion we can expand the wavefunctions in the form

$$\psi_n(\mathbf{r}) = \sum_{l=0}^{n-1} \sum_{m=-l}^l R_{nl}(r) Y_{lm}(\theta, \phi), \quad (7)$$

where the spherical harmonics satisfy

$$L^2 Y_{lm}(\theta, \phi) = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \sin \theta \frac{\partial}{\partial \theta} + \frac{1}{\sin^2 \theta} \frac{\partial^2}{\partial \phi^2} \right) Y_{lm}(\theta, \phi) = \hbar^2 l(l+1) Y_{lm}(\theta, \phi). \quad (8)$$

Thus, derive the differential equation for the radial part of the wavefunction as

$$\left[ \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l(l+1)}{r^2} + \frac{2Z}{a_0 r} - \frac{Z^2}{a_0^2 n^2} \right] R_{nl}(r) = 0. \quad (9)$$

(d) In terms of the dimensionless variable

$$x = \frac{2Zr}{a_0} \quad (10)$$

derive

$$\left[ \frac{d^2}{dx^2} + \frac{2}{x} \frac{d}{dx} - \frac{l(l+1)}{x^2} + \frac{1}{x} - \frac{1}{(2n)^2} \right] R_{nl}(x) = 0. \quad (11)$$

(e) For  $x \gg 1$  argue that we have

$$\left[ \frac{d^2}{dx^2} - \frac{1}{(2n)^2} \right] R_{nl}(x) = 0. \quad (12)$$

Solve this equation to learn the asymptotic behaviour of the radial wavefunction to be

$$R_{nl}(x) \sim e^{-\frac{x}{2n}} \quad \text{for} \quad x \gg 1. \quad (13)$$

(f) For  $x \ll 1$  argue that we have

$$\left[ \frac{1}{x^2} \frac{d}{dx} x^2 \frac{d}{dx} - \frac{l(l+1)}{x^2} \right] R_{nl}(x) = 0. \quad (14)$$

Solve this equation to learn the limiting behaviour of the radial wavefunction to be

$$R_{nl}(x) \sim x^l \quad \text{for} \quad x \ll 1. \quad (15)$$

(g) Use the above limiting forms to define

$$R_{nl}(x) = x^l e^{-\frac{x}{2n}} L(x), \quad (16)$$

and derive, in terms of

$$y = \frac{x}{n}, \quad (17)$$

$$\left[ y \frac{d^2}{dy^2} + \{(2l+1) + 1 - y\} \frac{d}{dy} + (n - l - 1) \right] L(y) = 0. \quad (18)$$

Compare this to the differential equation satisfied by the Laguerre polynomials,  $L_n^{(\alpha)}(y)$ , the Laguerre equation,

$$\left[ y \frac{d^2}{dy^2} + \{\alpha + 1 - y\} \frac{d}{dy} + n \right] L_n^{(\alpha)}(y) = 0. \quad (19)$$

Thus, derive

$$R_{nl}(r) = N \left( \frac{2Zr}{na_0} \right)^l e^{-\frac{Zr}{na_0}} L_{n-l-1}^{(2l+1)} \left( \frac{2Zr}{na_0} \right), \quad (20)$$

where  $N$  is a normalization constant.

(h) The normalization constant  $N$  is, in principle, determined using

$$\int_0^\infty r^2 dr |R_{nl}(r)|^2 = 1. \quad (21)$$

Verify that, the above statement does not, immediately, lead to the orthogonality relation for Laguerre polynomials,

$$\int_0^\infty dx x^\alpha e^{-x} L_n^{(\alpha)}(x) L_{n'}^{(\alpha)}(x) = \delta_{nn'} \frac{(n+\alpha)!}{n!}. \quad (22)$$

(i) Let us derive the Hellmann-Feynman theorem. Consider the energy eigenvalue equation

$$[H(\lambda) - E(\lambda)]|E, \lambda\rangle = 0 \quad (23)$$

and its adjoint

$$\langle E, \lambda | [H(\lambda) - E(\lambda)] = 0. \quad (24)$$

Differentiate with respect to  $\lambda$ :

$$\left( \frac{\partial E}{\partial \lambda} - \frac{\partial H}{\partial \lambda} \right) |E, \lambda\rangle + (E - H)|E, \lambda\rangle = 0, \quad (25)$$

and multiply with  $\langle E, \lambda |$  to obtain

$$\left\langle \frac{\partial H}{\partial \lambda} \right\rangle = \langle E, \lambda | \frac{\partial H}{\partial \lambda} | E, \lambda \rangle = \frac{\partial E}{\partial \lambda}, \quad (26)$$

which is the statement of the Hellmann-Feynman theorem.

(j) Use the Hellmann-Feynman theorem, by regarding  $\lambda$  as  $Z$ , in the hydrogenic atom to evaluate

$$\left\langle \frac{1}{r} \right\rangle_n = \int_0^\infty r^2 dr \frac{1}{r} |R_{nl}(r)|^2 = \frac{Z}{a_0 n^2}. \quad (27)$$

(k) Use the orthogonality relation of Laguerre polynomials in Eq. (22) in Eq. (27) to derive the normalization constant  $N$  as

$$N = \frac{2}{n^2} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}}. \quad (28)$$

Thus, derive the hydrogenic wavefunction

$$\psi_{nlm}(\mathbf{r}) = \frac{2}{n^2} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \sqrt{\frac{(n-l-1)!}{(n+l)!}} \left( \frac{2Zr}{na_0} \right)^l e^{-\frac{Zr}{na_0}} L_{n-l-1}^{(2l+1)} \left( \frac{2Zr}{na_0} \right) Y_{lm}(\theta, \phi). \quad (29)$$

2. In this problem we shall construct the eigenfunction  $\psi_{n,n-1,n-1}(\mathbf{r})$ .

(a) Since  $|n, n-1, n-1\rangle$  is in the highest possible  $l$  and  $m$ , we have

$$J_+^{(1)}|n, n-1, n-1\rangle = 0 \quad \text{and} \quad J_+^{(2)}|n, n-1, n-1\rangle = 0. \quad (30)$$

Thus, conclude that

$$L_+|n, n-1, n-1\rangle = 0 \quad \text{and} \quad \hbar n A_+|n, n-1, n-1\rangle = 0. \quad (31)$$

(b) Show that

$$Y_{n-1, n-1}(\theta, \phi) \sim \left( \frac{x + iy}{r} \right)^{n-1}. \quad (32)$$

Thus, construct the eigenfunction to have the form

$$\psi_{n, n-1, n-1}(r, \theta, \phi) = (x + iy)^{n-1} f_n(r). \quad (33)$$

(c) Show that

$$f_n(r) = C e^{-\frac{Zr}{na_0}}, \quad (34)$$

where  $C$  is a normalization constant. Thus, derive

$$\psi_{n, n-1, n-1}(r, \theta, \phi) = C (r \sin \theta e^{i\phi})^{n-1} e^{-\frac{Zr}{na_0}}. \quad (35)$$

(d) Requiring

$$\int d^3r |\psi_{n, n-1, n-1}(r, \theta, \phi)|^2 = 1, \quad (36)$$

which involves the integral

$$I_l = \frac{1}{2} \int_{-1}^1 dt (1 - t^2)^l, \quad (37)$$

determine the normalization constant (upto a phase) to be

$$|C| = \frac{2}{n^2} \left( \frac{Z}{a_0} \right)^{\frac{3}{2}} \left( \frac{2Z}{na_0} \right)^{n-1} \frac{1}{\sqrt{4\pi}} \frac{1}{2^{n-1}(n-1)!}. \quad (38)$$

Hint: Evaluate  $I_l$  using integration by parts to notice

$$I_l = \frac{2l}{2l+1} I_{l-1}, \quad (39)$$

and iterate this relation to yield

$$I_l = \frac{(2^l l!)^2}{(2l+1)!}. \quad (40)$$

(e) Verify that the solution is indeed

$$\psi_{n, n-1, n-1}(r, \theta, \phi) = R_{n, n-1}(r) Y_{n-1, n-1}(\theta, \phi). \quad (41)$$