3.012 Bonding-Structure: Recitation 2

1 Spherical Coordinates

Recall

- *volume of a spatial region* Ω*:* $\int_{\Omega} d\overrightarrow{r}$
- *integrals in spherical coordinates:*
  $\int_{space} f(\overrightarrow{r})d\overrightarrow{r} = \int_{r=0}^{r=+\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} f(r,\theta,\phi) r^2 \sin(\theta) dr d\theta d\phi$
- *orthogonality condition in spherical coordinates:*
  $\int_{space} \psi_a^*(\overrightarrow{r})\psi_b(\overrightarrow{r})d\overrightarrow{r} = 0$
- *In 3D, the probability of finding an electron* $\psi(\overrightarrow{r})$ *in the spatial region* $\begin{cases} r_{min} < r < r_{max} \\ \theta_{min} < \theta < \theta_{max} \\ \phi_{min} < \phi < \phi_{max} \end{cases}$ *is given by the integral* $\int_{r_{min}}^{r_{max}} \int_{\theta_{min}}^{\theta_{max}} \int_{\phi_{min}}^{\phi_{max}} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi) r^2 \sin(\theta) dr d\theta d\phi$ *(*ψ *must be normalized; that is,* $\int_{space} \psi^*(\overrightarrow{r})\psi(\overrightarrow{r})d\overrightarrow{r} = 1$*)*

Problem I

Which of the following statements are true? Explain.

(a) The volume of the spatial region $\begin{cases} r_{min} < r < r_{max} \\ \theta_{min} < \theta < \theta_{max} \\ \phi_{min} < \phi < \phi_{max} \end{cases}$ is given by $\left(\int_{r_{min}}^{r_{max}} r^2 dr\right) \times \left(\int_{\theta_{min}}^{\theta_{max}} \sin(\theta) d\theta\right) \times \left(\int_{\phi_{min}}^{\phi_{max}} d\phi\right)$

(b) The volume of a half-shell of outer radius R and thickness h is given by $\left(\int_{R-h}^{R} r^2 dr\right) \times \left(\int_0^{2\pi} \sin(\theta) d\theta\right) \times \left(\int_0^{\pi/2} d\phi\right)$

(c) Two wavefunctions $\psi_a(r)$ and $\psi_b(r)$ (which do not depend on θ and ϕ) are orthogonal if the integral $\int_0^{+\infty} \psi_a^*(r)\psi_b(r)r^2dr$ equals zero

(d) The probability of finding an electron of normalized wavefunction $\psi(r)$ (which does not depend on θ and ϕ) in the spatial region $r_{min} < r < r_{max}$ is given by the integral $\int_{r_{min}}^{r_{max}} \psi^*(r,\theta,\phi)\psi(r,\theta,\phi)r^2dr$

2 Expectation Values

Recall

- *correspondence principle (measurable quantity $\rightarrow$ operator): $x \rightarrow x$, $p_x \rightarrow -i\hbar\frac{\partial}{\partial x}$, etc...*
- *expectation value of the measurable quantity A: (i) use the correspondence principle to transform A into an operator (ii) calculate $\langle A\rangle = \int_{space} \psi^*(\overrightarrow{r})\{\hat{A}\psi(\overrightarrow{r})\}d\overrightarrow{r}$ (ψ must be normalized)*
- *Hamiltonian (energy operator): $\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\overrightarrow{r})$*
- *In spherical coordinates,*
  $\nabla^2 f(r,\theta,\phi) = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}f(r,\theta,\phi)\right)+\frac{1}{r^2\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial}{\partial\theta}f(r,\theta,\phi)\right)+\frac{1}{r^2\sin(\theta)}\frac{\partial^2}{\partial\phi^2}f(r,\theta,\phi)$
  (you do not need to remember this formula, but you have to know how to use it)

Problem II

Which of the following statements are true? Explain.

- *Expectation Values in 1D*

  (a1) The expectation value for the position of an electron in the normalized quantum state $\psi(x)$ is $\langle x\rangle = \int_{-\infty}^{+\infty} xn(x)dx$ where $n(x) = \psi^*(x)\psi(x)$ is the electron density

  (a2) In classical mechanics, the potential felt by an electron in the state $\left\{ \begin{array}{r} \text{position} = x_0 \\ \text{momentum} = p_0 \end{array} \right\}$ is equal to $V(x_0)$. In quantum mechanics, the potential felt by an electron in the normalized state {wavefunction=$\psi(x)$} is equal to $V(\langle x\rangle)$ where $\langle x\rangle$ is the expectation value for the position of the electron.

(a3) In classical mechanics, the kinetic energy of an electron in the state $\{x_0, y_0\}$ is equal to $\frac{p_0^2}{2m}$. In quantum mechanics, the expectation value for the kinetic energy of an electron in the normalized state $\psi(x)$ is equal to $\langle\frac{p^2}{2m}\rangle = \int_{-\infty}^{+\infty} \psi^*(x) \left\{-\frac{\hbar^2}{2m}(\frac{d}{dx}\psi(x))^2\right\} dx$

(a4) The expectation value for the kinetic energy of an electron in the normalized state $\psi(x)$ is equal to $\langle\frac{p^2}{2m}\rangle = \int_{-\infty}^{+\infty} \psi^*(x)\frac{1}{2m} \left\{-i\hbar\frac{d}{dx}\left(-i\hbar\frac{d}{dx}\psi(x)\right)\right\} dx$

(a5) In classical mechanics, the total energy of an electron in the state $\{x_0, y_0\}$ is equal to $E = \frac{p_0^2}{2m} + V(x_0)$. In quantum mechanics, the expectation value for the total energy of an electron in the normalized state $\psi(x)$ is equal to $\langle E\rangle = \int_{-\infty}^{+\infty} \psi^*(x)\hat{H}\psi(x)dx$

(a6) The expectation value of the measurable quantity A (quantum operator $\hat{A}$) for an electron in the normalized state $\psi(x)$ is always equal to the expectation value of A for an electron in the normalized state $e^{i\alpha}\psi(x)$ (where α is a real constant).

- *Expectation Values in 3D*

  (b1) The expectation value for the distance from the origin for an electron in the normalized state $\psi(r)$ (ψ does not depend on θ and ϕ) is given by $\langle r\rangle = 4\pi\int_0^{+\infty} rn(r)dr = 4\pi\int_0^{+\infty} r\psi^*(r)\psi(r)dr$

  (b2) The expectation value for the kinetic energy of an electron in the normalized state $\psi(r)$ (ψ does not depend on θ and ϕ) is given by $\langle\frac{p^2}{2m}\rangle = -\frac{2\pi\hbar^2}{m}\int_0^{+\infty} \psi^*(r)\frac{d}{dr}r^2\frac{d}{dr}\psi(r)dr$

3 Spectrum

Recall

- *eigenvalues of a electron in the presence of the nucleus of a hydrogen atom:* $E_n = -2.179 \times 10^{-18}\ J/n^2 = -13.60\ eV/n^2$ *(where n=1,2,3,4,...)*

Problem III

What is the meaning of the following diagram?

Source: Fig. 5.7 in Carroll, Bradley W., and Dale A. Ostlie. *An Introduction to Modern Astrophysics*. 2nd ed. San Francisco, CA: Pearson Addison-Wesley, 2007. ISBN: 0805304029.

(http://burro.astr.cwru.edu/Academics/Astr221/Light/spectra.html)