3.012 Bonding-Structure: Recitation 2

1 Spherical Coordinates

Recall

- *volume of a spatial region* $\Omega$: $\int_{\Omega} d^3 \mathbf{r}$
- *integrals in spherical coordinates*:
  \[ \int_{\text{space}} f(\mathbf{r}) d^3 \mathbf{r} = \int_{r=0}^{r=+\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} f(r, \theta, \phi) r^2 \sin(\theta) d\theta d\phi \]
- *orthogonality condition in spherical coordinates*:
  \[ \int_{\text{space}} \psi^*(\mathbf{r}) \psi(\mathbf{r}) d^3 \mathbf{r} = 0 \]

- *In 3D, the probability of finding an electron* $\psi(\mathbf{r})$ *in the spatial region* $\{ r_{\min} < r < r_{\max}, \theta_{\min} < \theta < \theta_{\max}, \phi_{\min} < \phi < \phi_{\max} \}$
  is given by the integral $\int_{r_{\min}}^{r_{\max}} \int_{\theta_{\min}}^{\theta_{\max}} \int_{\phi_{\min}}^{\phi_{\max}} \psi^*(r, \theta, \phi) \psi(r, \theta, \phi) r^2 \sin(\theta) d\theta d\phi$ ($\psi$ must be normalized; that is, $\int_{\text{space}} \psi^*(\mathbf{r}) \psi(\mathbf{r}) d^3 \mathbf{r} = 1$)

**Problem I**

Which of the following statements are true? Explain.

(a) The volume of the spatial region $\{ r_{\min} < r < r_{\max}, \theta_{\min} < \theta < \theta_{\max}, \phi_{\min} < \phi < \phi_{\max} \}$ 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 \( \theta \) and \( \phi \)) are orthogonal if the integral \( \int_0^{+\infty} \psi_a^*(r)\psi_b(r)r^2\,dr \) equals zero.

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

2 Expectation Values

Recall

- \textit{correspondence principle (measurable quantity \( \rightarrow \) operator):} \( x \rightarrow x, \ p_x \rightarrow -i\hbar \frac{\partial}{\partial x} \), etc...

- \textit{expectation value of the measurable quantity} \( A \): (i) use the \textit{correspondence principle} to transform \( A \) into an \textit{operator} (ii) calculate \( \langle A \rangle = \int_{\text{space}} \psi^* (\vec{r}) \{A \psi (\vec{r})\} \, d\vec{r} \) (\( \psi \) must be normalized)

- \textit{Hamiltonian (energy operator):} \( \hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V(\vec{r}) \)

- \textit{In spherical coordinates,}
\[
\nabla^2 f(r,\theta,\phi) = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 \frac{\partial}{\partial r} f(r,\theta,\phi) \right) + \frac{1}{r^2 \sin(\theta)} \frac{\partial}{\partial \theta} \left( \sin(\theta) \frac{\partial}{\partial \theta} f(r,\theta,\phi) \right) + \frac{1}{r^2 \sin^2(\theta)} \frac{\partial^2}{\partial \phi^2} f(r,\theta,\phi)
\]

(\textit{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.

- \textit{Expectation Values in 1D}

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

  (a2) In classical mechanics, the potential felt by an electron in the state \( \left\{ \begin{array}{l} \text{position} = x_0 \\ \text{momentum} = p_0 \end{array} \right\} \) is equal to \( V(x_0) \). In quantum mechanics, the potential felt by an electron in the normalized state \( \{ \text{wavefunction} = \psi(x) \} \) 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 \( \frac{\mathbf{p}^2}{2m} \). In quantum mechanics, the expectation value for the kinetic energy of an electron in the normalized state \( \psi(x) \) is equal to \( \langle \frac{\mathbf{p}^2}{2m} \rangle = \int_{-\infty}^{+\infty} \psi^* (x) \left\{ -\frac{\hbar^2}{2m} \left( \frac{d}{dx} \psi(x) \right)^2 \right\} dx \)

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

(a5) In classical mechanics, the total energy of an electron in the state \( \{x_0, y_0\} \) is equal to \( E = \frac{\mathbf{p}^2}{2m} + V(x_0) \). 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 \( \alpha \) 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 \( \psi(r) \) (\( \psi \) does not depend on \( \theta \) and \( \phi \)) is given by \( \langle r \rangle = 4\pi \int_0^{+\infty} r^n(r)dr = 4\pi \int_0^{+\infty} r^{n-1}r^n(r)\psi(r)rdr \)

  (b2) The expectation value for the kinetic energy of an electron in the normalized state \( \psi(r) \) (\( \psi \) does not depend on \( \theta \) and \( \phi \)) is given by \( \langle \frac{\mathbf{p}^2}{2m} \rangle = \frac{2\pi n^2}{m} \int_0^{+\infty} \psi^* (r) \frac{d}{dr}r^2 \frac{d}{dr}\psi(r)dr \)
3 Spectrum

Recall

- *eigenvalues of a electron in the presence of the nucleus of a hydrogen atom*: \( E_n = -2.179 \times 10^{-38} \frac{J}{n^2} = -13.60 \, eV/n^2 \) (where \( n=1,2,3,4,\ldots \))

Problem III

What is the meaning of the following diagram?

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