3.012 Bonding-Structure: Recitation 2 (Solutions)

1 Spherical Coordinates

Solution I

(a) <u>TRUE</u>
The volume $\mathcal{V}$ of a spatial region Ω is given by $\mathcal{V} = \int_\Omega d\overrightarrow{r}$.

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 thus

$\mathcal{V} = \int_{r_{min}}^{r_{max}} \int_{\theta_{min}}^{\theta_{max}} \int_{\phi_{min}}^{\phi_{max}} r^2 \sin(\theta) dr d\theta d\phi$
which can be rewritten as
$\mathcal{V} = \left(\int_{r_{min}}^{r_{max}} r^2 dr \right) \times \left(\int_{\theta_{min}}^{\theta_{max}} \sin(\theta) d\theta \right) \times \left(\int_{\phi_{min}}^{\phi_{max}} d\phi \right)$

(b) <u>FALSE</u>
A half-shell of outer radius R and thickness h can be defined as the spatial region
$\begin{cases} R - h < r < R \\ 0 < \theta < \pi/2 \\ 0 < \phi < 2\pi \end{cases}$
(remember that θ must always be in the range $0 < \theta < \pi$, and ϕ in the range $0 < \theta < 2\pi$)
Hence, from the preceding question, the volume of the half-shell is given by $\left(\int_{R-h}^{R} r^2 dr \right) \times$
$\left(\int_0^{\frac{\pi}{2}} \sin(\theta) d\theta \right) \times \left(\int_0^{2\pi} d\phi \right)$

(c) <u>TRUE</u>
The orthogonality condition between $\psi_a(r)$ and $\psi_b(r)$ can be written as:
$\int_{space} \psi_a^*(r) \psi_b(r) d\overrightarrow{r} = 0$ (note that there is no arrow on r).
Using spherical coordinates, we obtain:

$$\int_{r=0}^{r=+\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} \psi_a^*(r)\psi_b(r)r^2 \sin(\theta) dr d\theta d\phi \quad = \quad 0$$

$$\left\{ \int_{r=0}^{r=+\infty} \psi_a^*(r)\psi_b(r)r^2 dr \right\} \left\{ \int_{\theta=0}^{\theta=\pi} \sin(\theta)d\theta \right\} \left\{ \int_{\phi=0}^{\phi=2\pi} d\phi \right\} = 0$$

$\int_{\theta=0}^{\theta=\pi} \sin(\theta)d\theta$ and $\int_{\phi=0}^{\phi=2\pi} d\phi$ are constant. Thus, the orthogonality condition can be rewritten $\int_{r=0}^{r=+\infty} \psi_a^*(r)\psi_b(r)r^2 dr = 0$.

(d) <u>FALSE</u>

The region $r_{min} < r < r_{max}$ is in fact defined as $\begin{cases} r_{min} < r < r_{max} \\ 0 < \theta < \pi \\ 0 < \phi < 2\pi \end{cases}$

The probability of finding an electron of wavefunction $\psi(r)$ (no arrow on r) in the spatial region $r_{min} < r < r_{max}$ is thus given by:

$$\int_{r_{min}}^{r_{max}} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} \psi^*(r)\psi(r)r^2 \sin(\theta) dr d\theta d\phi$$

$$= \left\{ \int_{r=0}^{r=+\infty} \psi^*(r)\psi(r)r^2 dr \right\} \left\{ \int_{\theta=0}^{\theta=\pi} \sin(\theta)d\theta \right\} \left\{ \int_{\phi=0}^{\phi=2\pi} d\phi \right\}$$

$$= 4\pi \int_{r=0}^{r=+\infty} \psi^*(r)\psi(r)r^2 dr$$

$$\neq \int_{r=0}^{r=+\infty} \psi^*(r)\psi(r)r^2 dr$$

2 Expectation Values

Solution II

- *Expectation Values in 1D*

  (a1) <u>TRUE</u>

  i) classical quantity: x

  ii) correspondence principle: $x \to x$

  iii) quantum operator: $\hat{x} = x$

  iv) expectation value $\langle x \rangle = \int_{-\infty}^{+\infty} \psi^*(x)\{x\psi(x)\}dx$.

  Using the definition of the electron density $n(x) = \psi^*(x)\psi(x)$, the expectation value for the position of the electron can be rewritten as $\langle x \rangle = \int_{-\infty}^{+\infty} xn(x)dx$.

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The expectation value of the observable x is thus the integral x weighted by the electron density ($\equiv$electron probability).

(a2) <u>FALSE</u>

i) classical quantity: $V(x)$

ii) correspondence principle: $x \to x$

iii) quantum operator: $\widehat{V(x)} = V(x)$

iv) expectation value $\langle V(x) \rangle = \int_{-\infty}^{+\infty} \psi^*(x)\{V(x)\psi(x)\}dx = \int_{-\infty}^{+\infty} V(x)\psi^*(x)\psi(x)dx$
which is different from $V(\langle x \rangle) = V\left(\int_{-\infty}^{+\infty} x\psi^*(x)\psi(x)dx\right)$

Conclusion: $V(\langle x \rangle) \neq \langle V(x) \rangle$.

In words, the expectation value of the potential ($\equiv$average of the potential weighted by the electron density) differs from the potential at the average position of the particle.

(a3) <u>FALSE</u>

i) classical quantity: $p^2/2m$

ii) correspondence principle: $p \to \hat{p} = -i\hbar\frac{d}{dx}$

iii) quantum operator: we need to apply $-i\hbar\frac{d}{dx}$ twice

$$\hat{p}\psi(x) = -i\hbar\frac{d}{dx}\psi(x)$$
$$\hat{p}(\hat{p}\psi(x)) = -i\hbar\frac{d}{dx}\left(-i\hbar\frac{d}{dx}\psi(x)\right)$$
$$\hat{p}(\hat{p}\psi(x)) = (-i)^2\hbar^2\frac{d}{dx}\frac{d}{dx}\psi(x)$$
$$\hat{p}(\hat{p}\psi(x)) = -\hbar^2\frac{d^2}{dx^2}\psi(x)$$

Thus, $\hat{p}^2/2m = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2}$

iv) expectation value $\langle p^2/2m \rangle = \int_{-\infty}^{+\infty} \psi^*(x)\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)\}dx$ which is different from
$\int_{-\infty}^{+\infty} \psi^*(x)\left\{-\frac{\hbar^2}{2m}(\frac{d}{dx}\psi(x))^2\right\}dx$

(a4) <u>TRUE</u>

$\frac{\hat{p}^2}{2m}\psi(x)$ can also be written as $\frac{1}{2m}\left\{-i\hbar\frac{d}{dx}\left(-i\hbar\frac{d}{dx}\psi(x)\right)\right\}$

Thus $\langle p^2/2m \rangle = \int_{-\infty}^{+\infty} \psi^*(x)\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x)\}dx = \int_{-\infty}^{+\infty} \psi^*(x)\frac{1}{2m}\left\{-i\hbar\frac{d}{dx}\left(-i\hbar\frac{d}{dx}\psi(x)\right)\right\}dx$

(a5) <u>TRUE</u>

i) classical quantity: $E = p^2/2m + V(x)$

ii) correspondence principle: $x \to x$, $p \to -i\hbar\frac{d}{dx}$

iii) quantum operator: from the preceding question, it can be seen that
$\hat{E} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + V(x) = \hat{H}$

iv) expectation value: $\langle E \rangle = \int_{-\infty}^{+\infty} \psi^*(x)\left\{-\frac{\hbar^2}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x)\right\}dx = \int_{-\infty}^{+\infty} \psi^*(x)\hat{H}\psi(x)dx$

(a6) <u>TRUE</u>

We need to apply the "expectation-value procedure" to both $\psi(x)$ and $e^{i\alpha}\psi(x)$.

I) $\psi(x)$

i) classical quantity: A

ii) quantum operator: $\hat{A}$

iii) expectation value: $\langle A \rangle = \int_{-\infty}^{+\infty} \psi^*(x)\{\hat{A}\psi(x)\}dx$

II) $e^{i\alpha}\psi(x)$

i) classical quantity: A

ii) quantum operator: $\hat{A}$

iii) expectation value: $\langle A \rangle = \int_{-\infty}^{+\infty} \left\{e^{i\alpha}\psi(x)\right\}^* \{\hat{A}e^{i\alpha}\psi(x)\}dx$

Since $\hat{A}$ is linear [1], $\hat{A}e^{i\alpha}\psi(x) = e^{i\alpha}\hat{A}\psi(x)$.

Thus,

$$
\begin{aligned}
\langle A \rangle &= \left(e^{i\alpha}\right)^* e^{i\alpha} \int_{-\infty}^{+\infty} \psi^*(x)\{\hat{A}\psi(x)\}dx \\
&= \left|e^{i\alpha}\right|^2 \int_{-\infty}^{+\infty} \psi^*(x)\{\hat{A}\psi(x)\}dx \\
&= \int_{-\infty}^{+\infty} \psi^*(x)\{\hat{A}\psi(x)\}dx
\end{aligned}
$$

(1)

The two results are identical. The expectation value of the measurable quantity 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 $e^{i\alpha}\psi(x)$.

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[1] $\hat{A}$ is indeed obtained from A by the correspondence principle and, as such, is generally linear and Hermitian (lecture 4)

- *Expectation Values in 3D*

  (b1) <u>FALSE</u>

  i) classical quantity: r

  ii) correspondence principle: $r \to r$

  iii) quantum operator: $\hat{r} = r$

  iv) expectation value:

  $$
  \begin{aligned}
  \langle r \rangle &= \int_{r=0}^{r=+\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} \psi^*(r)\{r\psi(r)\}r^2 \sin(\theta)drd\theta d\phi \\
  &= \left\{ \int_{r=0}^{r=+\infty} \psi^*(r)\psi(r)r^3 dr \right\} \left\{ \int_{\theta=0}^{\theta=\pi} \sin(\theta)d\theta \right\} \left\{ \int_{\phi=0}^{\phi=2\pi} d\phi \right\} \\
  &= 4\pi \int_{r=0}^{r=+\infty} \psi^*(r)\psi(r)r^3 dr \neq 4\pi \int_{r=0}^{r=+\infty} \psi^*(r)\psi(r)r dr
  \end{aligned}
  $$

  (b1) <u>TRUE</u>

  i) classical quantity: $p^2/2m$

  ii) correspondence principle: $p \to -i\hbar\nabla$

  iii) quantum operator: $\hat{p}/2m = -\frac{\hbar^2}{2m}\nabla^2$

  iv) expectation value: $\langle \frac{p^2}{2m} \rangle = \int_{r=0}^{r=+\infty} \int_{\theta=0}^{\theta=\pi} \int_{\phi=0}^{\phi=2\pi} \psi^*(r)\{-\frac{\hbar^2}{2m}\nabla^2\psi(r)\}r^2 \sin(\theta)drd\theta d\phi$

  Since $\psi(r)$ depends only on r, $\nabla^2\psi(r) = \frac{1}{r^2}\frac{d}{dr}r^2\frac{d}{dr}\psi(r)$.

  Thus $\langle \frac{p^2}{2m} \rangle = -\frac{\hbar^2}{2m} \left\{ \int_{r=0}^{r=+\infty} \psi^*(r)\frac{d}{dr}r^2\frac{d}{dr}\psi(r)dr \right\} \left\{ \int_{\theta=0}^{\theta=\pi} \sin(\theta)d\theta \right\} \left\{ \int_{\phi=0}^{\phi=2\pi} d\phi \right\}$

  $\langle \frac{p^2}{2m} \rangle = -\frac{2\pi\hbar^2}{m} \int_0^{+\infty} \psi^*(r)\frac{d}{dr}r^2\frac{d}{dr}\psi(r)dr$

3 Spectrum

Solution III

The quantized energy levels for an electron bond to a proton (hydrogen atom) are shown together with the allowed energy transitions (absorption and emission lines). The spectral lines associated with transitions from the eigenstates n=1,2 and 3 are referred to as the "Lyman series", the "Balmer series" and the "Paschen series", respectively. The Balmer series was actually the first to be observed because it corresponds to absorption in the visible and near ultra-violet frequency range.