Assignment (10)

① $\hat{H} = \sum_{A=1}^{P} -\frac{\hbar^2}{2M_A}\nabla_A^2 + \sum_{i=1}^{N} -\frac{\hbar^2}{2m_e}\nabla_i^2 + \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B e^2}{4\pi\varepsilon_0|\vec{R}_A-\vec{R}_B|} + \frac{1}{2}\sum_{i\neq j}\frac{e^2}{4\pi\varepsilon_0|\vec{r}_i-\vec{r}_j|} - \sum_{A=1}^{P}\sum_{i=1}^{N}\frac{Z_A e^2}{4\pi\varepsilon_0|\vec{R}_A-\vec{r}_i|}$

② $\hat{H} = \sum_{A=1}^{P} -\frac{\nabla_A^2}{2M_A} + \sum_{i=1}^{N} -\frac{\nabla_i^2}{2} + \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{|\vec{R}_A-\vec{R}_B|} + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i-\vec{r}_j|} - \sum_{A=1}^{P}\sum_{i=1}^{N}\frac{Z_A}{|\vec{R}_A-\vec{r}_i|}$

③ $\hat{H}_{el} = \sum_{i=1}^{N} -\frac{\nabla_i^2}{2} + \frac{1}{2}\sum_{A\neq B}\frac{Z_A Z_B}{|\vec{R}_A-\vec{R}_B|} + \frac{1}{2}\sum_{i\neq j}\frac{1}{|\vec{r}_i-\vec{r}_j|} - \sum_{A=1}^{P}\sum_{i=1}^{N}\frac{Z_A}{|\vec{R}_A-\vec{r}_i|}$

$\hat{H}_{el}\Psi_{el}\{\vec{r}_1,\dots,\vec{r}_N|\vec{R}_1,\dots,\vec{R}_P\} = E\{\vec{R}_1,\dots,\vec{R}_P\}\Psi_{el}\{\vec{r}_1,\dots,\vec{r}_N|\vec{R}_1,\dots,\vec{R}_P\}$

④ $\left[\sum_{A=1}^{P} -\frac{\nabla_A^2}{2M_A} + E\{\vec{R}_1,\dots,\vec{R}_P\}\right]\chi_{nucl.}\{\vec{R}_1,\dots,\vec{R}_P\} = E_{TOTAL}\,\chi_{nucl.}\{\vec{R}_1,\dots,\vec{R}_P\}$.

⑤ The BO Approximation is more important for light atoms. F is the lightest element in the options, so it is less justified to use BO approximation in c) UF_6. For heavier the atoms, it is more important to include relativistic effects, so d) $XeCl_2$

⑥ $E_n = -\frac{m_e Z^2 e^2}{8\varepsilon_0^2 h^2 n^2}$; $\hat{H} = -\frac{\hbar^2}{2m_e}\nabla_e^2 - \frac{Ze}{4\pi\varepsilon_0|\vec{r}-\vec{R}|}$

$E_n = -\frac{m_e Z^2 e^2}{32\varepsilon_0^2\pi^2\hbar^2 n^2}$

a) $\frac{\partial E_n}{\partial\hbar} = \int\Psi_{nlm}^*\{r,\theta,\phi\}\frac{\partial\hat{H}}{\partial\hbar}\Psi_{nlm}\{r,\theta,\phi\}\,d\vec{r}$

$(-2)\left(-\frac{m_e Z^2 e^2}{32\varepsilon_0^2\pi^2 n^2}\right)\left(\frac{1}{\hbar^3}\right) = \int\Psi_{nlm}^*\{r,\theta,\phi\}\left[-\frac{2\hbar}{2m_e}\nabla_e^2\right]\Psi_{nlm}\{r,\theta,\phi\}\,d\vec{r}$

$\left(-\frac{m_e}{\hbar}\right)\left(\frac{m_e Z^2 e^2}{16\varepsilon_0^2\pi^2 n^2\hbar^3}\right) = \int\Psi_{nlm}^*\{r,\theta,\phi\}\nabla_e^2\Psi_{nlm}\{r,\theta,\phi\}\,d\vec{r}$

$\langle\nabla^2\rangle = -\frac{m_e^2 Z^2 e^2}{16\varepsilon_0^2\pi^2 n^2\hbar^4}$

b) $\langle\hat{r}\rangle_{1,0,0} = \int\Psi_{1,0,0}^*\{r,\theta,\phi\}\,r\,\Psi_{1,0,0}\{r,\theta,\phi\}\,d\vec{r} = \left(\sqrt{Z^3/\pi}\right)^2\int r e^{-2Zr}\,d\vec{r}$

$= \left(\sqrt{\frac{Z^3}{\pi}}\right)^2\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\int_0^{\infty}dr(r^2\sin\theta)(re^{-2Zr}) = (Z^3/\pi)(2\pi)(-\cos\theta|_0^{\pi})\int_0^{\infty}dr\,r^3 e^{-2Zr}$

$= Z^3(2)(+1+1)\left(3!/(2Z)^4\right) = \frac{4Z^3(3)(2)}{2^4 Z^4} = \frac{3}{2Z}$

$\langle\hat{r}\rangle_{2,1,0} = \int\Psi_{2,1,0}^*\{r,\theta,\phi\}\,r\,\Psi_{2,1,0}\{r,\theta,\phi\}\,d\vec{r} = (Z^3/2^5\pi)\int(Zr)e^{-Zr/2}\cos\theta\; r\cdot(Zr)e^{-Zr/2}\cos\theta\,d\vec{r}$

$= (Z^3/2^5\pi)Z^2\int_0^{2\pi}d\phi\int_0^{\pi}d\theta\int_0^{\infty}dr\left[r^3 e^{-Zr}\cos^2\theta\,(r^2\sin\theta)\right]$

$= \left(\frac{Z^5}{2^5\pi}\right)(2\pi)\left[\int_0^{\pi}d\theta\cos^2\theta\sin\theta\right]\left[\int_0^{\infty}dr\,r^5 e^{-Zr}\right]$ $\quad u = \cos\theta$, $du = -\sin\theta\,d\theta$

$= (Z^5/2^4)\left[\int_0^{\pi}u^2(-du)\right]\left[\frac{5!}{Z^6}\right] = \left(\frac{5\times4\times3\times2}{2^4\times Z}\right)\left[-\frac{\cos^3\theta}{3}\right]_0^{\pi} = \left(\frac{5}{2Z}\right)\left(-(-1)^3+(1)^3\right) = \frac{5}{Z}$

c) $\langle\hat{r}\rangle_{1,0,0} = 1.5$ a.u.

$\Psi_{1,0,0} = \sqrt{\frac{1}{\pi}}\,e^{-r}$

$P_{1s}\{r\} = \int_0^{\pi}d\theta\int_0^{2\pi}d\phi\left[\Psi_{1,0,0}^*\{r,\theta,\phi\}\Psi_{1,0,0}\{r,\theta,\phi\}\right][r^2\sin\theta]$

$= \int_0^{\pi}d\theta\int_0^{2\pi}d\phi\left(\frac{1}{\pi}\right)[e^{-2r}][r^2\sin\theta] = \left(\frac{r^2e^{-2r}}{\pi}\right)(-\cos\theta|_0^{\pi})(2\pi) = (r^2e^{-2r})(+1+1) = 2r^2e^{-2r}$

$\frac{dP_{1s}\{r\}}{dr} = 0$ → derivative = 0 when the probability is a max.

$2(2re^{-2r} - 2r^2e^{-2r}) = 0$

$\underbrace{(r-r^2)}_{=0}\underbrace{(e^{-2r})}_{\text{never}=0} = 0$

$r = r^2$ → $r = 1$ a.u.

the most probable r is smaller than mean r, so distribution is skewed to the left, and extends to infinity

d) $\Psi_{1s}\{r,\theta,\phi\} = \sqrt{2^3/\pi}\;e^{-2r}$

$\langle\hat{V}\rangle = \langle-\frac{Z}{r}\rangle = \langle-\frac{2}{r}\rangle = \int_0^{\infty}dr\int_0^{\pi}d\theta\int_0^{2\pi}d\phi\,(2^3/\pi)(e^{-4r})(-\frac{2}{r})(r^2\sin\theta)$

$= \left[\int_0^{\infty}dr\,(re^{-4r})\right][2^3/\pi][-2]\left[\int_0^{\pi}d\theta(\sin\theta)\right][2\pi]$

$= \left[\frac{1}{4^2}\right][8][-4][-\cos\theta|_0^{\pi}] = (-2)(1+1) = -4$ a.u.

e) $\langle\hat{T}\rangle + \langle\hat{V}\rangle = \langle\hat{H}\rangle = E_n = -Z^2/2n^2$

$\langle\hat{T}\rangle = -2^2/2(1)^2 - \langle\hat{V}\rangle = -2$ a.u. $+ 4$ a.u $= 2$ a.u.