Homework 3, solutions

problem 1, solution

a) The atomic orbitals $\phi_{n\ell m}(\vec{r})$ with $n=2, \ell=1$ are

$$\phi_{211} = -\sqrt{\frac{3}{8\pi}}\, R_{21}(r) \sin\theta\, e^{i\phi}$$

$$\phi_{210} = \sqrt{\frac{3}{4\pi}}\, R_{21}(r) \cos\theta$$

$$\phi_{21-1} = \sqrt{\frac{3}{8\pi}}\, R_{21}(r) \sin\theta\, e^{-i\phi}$$

All these orbitals are degenerate in energy.

$\phi_{210} = \sqrt{\frac{3}{4\pi}}\, R_{21}(r) \frac{z}{r}$ is real. It has rotational symmetry about the z-axis. Upon reflection about the x-y plane the wavefunction changes sign. The amplitude in any direction depends as $\cos\theta$ on the angle θ this direction makes with the z-axis. It is also called the p_z-orbital.

Linear superposition of ϕ_{211} and ϕ_{21-1} also can yield real wave functions,

$$\frac{1}{\sqrt{2}}\left(\phi_{21-1} - \phi_{211}\right) = \sqrt{\frac{3}{8\pi}}\, \frac{2}{\sqrt{2}} R_{21}(r) \sin\theta \cos\phi = \sqrt{\frac{3}{4\pi}}\, R_{21}(r) \frac{x}{r} = \underline{p_x \text{ orbital}}$$

$$\frac{i}{\sqrt{2}}\left(\phi_{211} + \phi_{21-1}\right) = \sqrt{\frac{3}{8\pi}}\, \frac{2}{\sqrt{2}} R_{21}(r) \sin\theta \sin\phi = \sqrt{\frac{3}{4\pi}}\, R_{21}(r) \frac{y}{r} = \underline{p_y \text{-orbital}}$$

These two orbitals have rotational symmetry about the x- and y-axis, respectively and behave with respect to the x- and y-axis as ϕ_{210} behaves with respect to the z-axis.

b) $\phi_{210} = \sqrt{\frac{3}{4\pi}}\, R_{21}(r) \cos\theta$, $\phi_{200} = \frac{1}{\sqrt{4\pi}} R_{20}(r)$.

Let $\psi_A = \frac{1}{\sqrt{2}}\left(\phi_{200} + \phi_{210}\right) = \frac{1}{\sqrt{2}}\left(\lambda + \mu\cos\theta\right)$, where $\lambda = \frac{1}{\sqrt{4\pi}} R_{20}(r)$ and $\mu = \sqrt{\frac{3}{4\pi}}\, R_{21}(r)$. λ and μ do not depend on θ or ϕ.

Let $\psi_B = \frac{1}{\sqrt{2}}\left(\phi_{200} - \phi_{210}\right) = \frac{1}{\sqrt{2}}\left(\lambda - \mu\cos\theta\right)$.

Both Ψ_A and Ψ_B have rotational symmetry about the z-axis. We can obtain Ψ_B from Ψ_A by reflecting through the x-y plane. The square of the amplitude of Ψ_A is larger in the positive z-direction than in the negative z-direction. This orbital extends further along the positive than along the negative z-direction. The amplitude in any direction at a given radius r depends as $A + u\cos\theta$ on the angle θ this direction makes with the z-axis.

We can easily construct orbitals that behave with respect to the x- and y-axis as Ψ_A and Ψ_B behaves with respect to the z-axis by forming linear combinations of equal weight of the p_x-orbital and ϕ_{200} and of the p_y-orbital and ϕ_{200}.

problem 2, solution

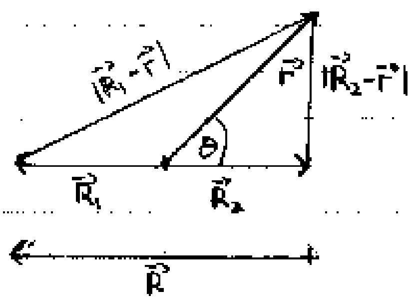
a) The Hamiltonian H for the H_2^+ molecule is

$$H = \frac{P_1^2}{2M_1} + \frac{P_2^2}{2M_2} + \frac{P_e^2}{2m} + \frac{e^2}{|\vec{R}_1-\vec{R}_2|} - \frac{e^2}{|\vec{R}_1-\vec{r}|} - \frac{e^2}{|\vec{R}_2-\vec{r}|} . \qquad M_1 = M_2 = m_p , \; m = m_e .$$

Let $\vec{R}_{cm} = \dfrac{M_1\vec{R}_1 + M_2\vec{R}_2}{M_1+M_2}$, $\vec{R} = \vec{R}_1 - \vec{R}_2$.

Then

$$H = \frac{P_{cm}^2}{2M} + \frac{P^2}{2\mu} + \frac{P_e^2}{2m} + \frac{e^2}{R} - \frac{e^2}{|\vec{R}_1-\vec{r}|} - \frac{e^2}{|\vec{R}_2-\vec{r}|} . \qquad M = M_1+M_2 , \; \mu = \frac{M_1M_2}{M_1+M_2} .$$



$$|\vec{R}_1-\vec{r}| = \left|\frac{\vec{R}}{2}-\vec{r}\right| = \left[\left(\frac{R}{2}\right)^2 + r^2 + Rr\cos\theta\right]^{1/2} .$$

$$|\vec{R}_2-\vec{r}| = \left|\frac{\vec{R}}{2}+\vec{r}\right| = \left[\left(\frac{R}{2}\right)^2 + r^2 - Rr\cos\theta\right]^{1/2} .$$

Therefore

$$H = \frac{P_{cm}^2}{2M} + \frac{P^2}{2\mu} + \frac{P_e^2}{2m} + \frac{e^2}{R} + V(\vec{R}, r) .$$

If the CM of the two nuclei is fixed, then the eigenvalue equation for H becomes

$$\left[-\frac{\hbar^2}{2\mu}\nabla_R^2 - \frac{\hbar^2}{2m}\nabla_r^2 + \frac{e^2}{R} + V(\vec{R},\vec{r})\right]\Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R}) .$$

b) Let $\Psi(\vec{r},\vec{R}) = \chi(\vec{R})\,\phi(\vec{R},\vec{r})$.

Inserting this form into the above eigenvalue equation we have

$$-\frac{\hbar^2}{2\mu}\left(\vec{\nabla}_R\cdot\left(\chi(\vec{R})\vec{\nabla}_R\phi(\vec{R},\vec{r}) + \phi(\vec{R},\vec{r})\vec{\nabla}_R\chi(\vec{R})\right)\right) - \frac{\hbar^2}{2m}\chi(\vec{R})\nabla_r^2\phi(\vec{r},\vec{R}) + \frac{e^2}{R}\chi(\vec{R})\phi(\vec{r},\vec{R})$$

$$+ V(\vec{R},\vec{r})\chi(\vec{R})\phi(\vec{r},\vec{R}) = E\,\phi(\vec{r},\vec{R})\,\chi(\vec{R}) .$$

$$-\frac{\hbar^2}{2\mu}\left(\chi(\vec{R})\nabla_R^2\phi(\vec{R},\vec{r}) + 2\vec{\nabla}_R\chi(\vec{R})\cdot\vec{\nabla}_R\phi(\vec{R},\vec{r}) + \phi(\vec{R},\vec{r})\nabla_R^2\chi(\vec{R})\right) + \frac{e^2}{R}\phi(\vec{r},\vec{R})\chi(\vec{R})$$

$$-\frac{\hbar^2}{2m}\chi(\vec{R})\nabla_r^2\phi(\vec{r},\vec{R}) + V(\vec{R},\vec{r})\chi(\vec{R})\phi(\vec{R},\vec{r}) = E\,\phi(\vec{r},\vec{R})\chi(\vec{R}).$$

$$-\frac{\hbar^2}{2\mu}\frac{1}{\phi}\nabla_R^2\phi - \frac{\hbar^2}{2\mu}\frac{1}{\phi\chi}\vec{\nabla}_R\chi\cdot\vec{\nabla}_R\phi - \frac{\hbar^2}{2\mu}\frac{1}{\chi}\nabla_R^2\chi - \frac{\hbar^2}{2m}\frac{1}{\phi}\nabla_r^2\phi + \frac{e^2}{R} + V - E = 0.$$

If we neglect terms that contain derivatives of $\phi(\vec{r},\vec{R})$ with respect to $\vec{R}$ we have

$$-\frac{\hbar^2}{2\mu}\frac{1}{\chi(R)}\nabla_R^2\chi(\vec{R}) - \frac{\hbar^2}{2m}\frac{1}{\phi(\vec{r},\vec{R})}\nabla_r^2\phi(\vec{r},\vec{R}) + V(\vec{r},\vec{R}) + \frac{e^2}{R} - E = 0.$$

For this equation to hold for all $\vec{r}$ and R

$$-\frac{\hbar^2}{2m}\frac{1}{\phi(\vec{r},\vec{R})}\nabla_r^2\phi(\vec{r},\vec{R}) + V(\vec{r},\vec{R}) = E_e(\vec{R}),$$ i.e. it must be a function of $\vec{R}$ only. $V(\vec{r},\vec{R}) = V(r,R,\theta)$, so $E_e(\vec{R}) = E_e(R)$.

We then have

$$\left[-\frac{\hbar^2}{2\mu}\vec{\nabla}_R^2\chi(R) + \frac{e^2}{R} + E_e(R)\right]\chi(\vec{R}) = E\,\chi(\vec{R}).$$

This is the equation of a particle of mass μ moving in a central potential.

We can write $\chi(\vec{R}) = \frac{u(R)}{R}Y_{\ell m}(\theta\phi)$,

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial R^2} + \frac{e^2}{R} + E_e(R) + \frac{\ell(\ell+1)\hbar^2}{2\mu R^2}\right]u(R) = 0.$$

For the ground state we have $\ell = 0$ and therefore

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2} + \frac{e^2}{R} + E_e(R)\right]u(R) = E_R\,u(R).$$

problem 3, solution

The radial equation describing the motion of the nuclei is

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+V(r)+\frac{\ell(\ell+1)\hbar^2}{2\mu r^2}\right]u_{v\ell}(r)=E_{v\ell}u_{v\ell}(r).$$

$$V(r)=-2D\left[\frac{a_0}{r}-\frac{a_0^2}{r^2}\right].$$

To find an extremum, set $\frac{\partial V(r)}{\partial r}=0$. $-2D\left[\frac{-a_0}{r^2}+\frac{2a_0^2}{r^3}\right]=0$, $r=2a_0=r_0$.

As $r\to 0$ $V(r)\to\infty$, As $r\to\infty$ $V(r)\to 0$. There is only one extremum, it must be a minimum.

Near r_0 we write: $V(r)=V(r_0)+\frac{1}{2}\left.\frac{d^2V(r)}{dr^2}\right|_{r_0}(r-r_0)^2$

$$=-2D\left[\frac{a_0}{2a_0}-\frac{a_0^2}{4a_0^2}\right]-\frac{1}{2}2D\left[\frac{2a_0}{(2a_0)^3}-\frac{6a_0^2}{(2a_0)^4}\right](r-2a_0)^2$$

$$=-\frac{1}{2}D+\frac{D}{8a_0^2}(r-2a_0)^2=-V_0+\frac{1}{2}\mu\omega^2(r-2a_0)^2.$$

Set $r'=r-2a_0$. Then $V(r')=-V_0+\frac{1}{2}\mu\omega^2r'^2$.

$\frac{1}{2}\mu\omega^2=\frac{D}{8a_0^2}$, $\omega^2=\frac{D}{4a_0^2\mu}$.

The vibrational energies are given by $E_v=-V_0+(v+\frac{1}{2})\hbar\omega$.

The vibrational-rotational energies are given by

$$E_{v\ell}=-V_0+(v+\tfrac{1}{2})\hbar\omega+\frac{\ell(\ell+1)\hbar^2}{8\mu a_0^2}=-V_0+(v+\tfrac{1}{2})\hbar\omega+Bh\,\ell(\ell+1),$$

with $B=\frac{1}{32\pi^2\mu a_0^2}$.

problem 4, solution

Let $K_0^2 = \frac{2\mu}{\hbar^2} V_0$ and $k^2 = \frac{2\mu}{\hbar^2} E$ if $E > 0$ and $\rho^2 = -\frac{2\mu}{\hbar^2} E$ if $E < E_0$

a) For $E > 0$ we have

$$\left(\frac{\partial^2}{\partial r^2} - \frac{\ell(\ell+1)}{r^2} - U(r) + k^2\right) U_{k\ell}(r) = 0 ;$$

with $U(r) = -k_0^2 \quad r < r_0$, $U(r) = 0 \quad r > r_0$.

For $E < 0$ we have

$$\left(\frac{\partial^2}{\partial \rho^2} - \frac{\ell(\ell+1)}{r^2} - U(r) - \rho^2\right) U_{k\ell}(r) = 0 .$$

The boundary conditions are:
$U_{k\ell}(0) = 0$, $U_{k\ell}(r)$ and $\frac{dU_{k\ell}(r)}{dr}$ are continuous at $r = r_0$, $U_{k\ell}(\infty) =$ finite.

b) $\left[\frac{\partial^2}{\partial r^2} + \left(K_0^2 + k^2\right)\right] U_0(r) = 0$, $\quad U_0(r) = C_1 \sin\left(\sqrt{K_0^2 + k^2}\, r\right)$, $r < r_0$.

$\left[\frac{\partial^2}{\partial r^2} - \rho^2\right] U_0(r) = 0$, $\quad U_0(r) = C_2 e^{-\rho r}$, $r > r_0$.

$$\left.\begin{aligned} &C_1 \sin\left(\sqrt{K_0^2 - k^2}\, r_0\right) = C_2 e^{-\rho r_0} \\ &\sqrt{K_0^2 - k^2}\, C_1 \cos\left(\sqrt{K_0^2 - k^2}\, r_0\right) = -\rho C_2 e^{-\rho r_0} \end{aligned}\right\} \text{Boundary conditions}$$

Therefore

$$\tan \sqrt{K_0^2 + k^2}\, r_0 = \frac{-\sqrt{K_0^2 + k^2}}{\rho} .$$

This is the condition k^2 and therefore E has to satisfy in order for the differential equation to have a solution.

c) $\left[\frac{\partial^2}{\partial r^2} + K^2\right] U_0(r) = 0 \qquad U_0 = B \sin K r$, $r < r_0$.

$\left[\frac{\partial^2}{\partial r^2} + k^2\right] U_0(r) = 0 \qquad U_0 = A \sin\left(k r + \delta_0\right)$, $r > r_0$.

$$\left.\begin{aligned} &B \sin K r_0 = A \sin(k r_0 + \delta_0) \\ &K B \cos K r_0 = A k \cos(k r_0 + \delta_0) \end{aligned}\right\} \text{Boundary conditions}$$

Therefore

$$\tan K r_0 = \frac{K}{k} \tan(k r_0 + \delta_0) , \quad \delta_0 = \tan^{-1}\left(\frac{k}{K} \tan K r_0\right) - k r_0 .$$

$$B^2 \sin^2 \varkappa r_0 = \sin^2(kr_0+\delta_0), \quad A=1,$$

$$\frac{1}{B^2\sin^2\varkappa r_0} = 1+\frac{\varkappa^2}{k^2}\cot^2(\varkappa r_0), \qquad \left(\frac{1}{\sin^2 x} = 1+\cot^2 x\right)$$

$$\frac{1}{B^2} = \sin^2(\varkappa r_0)+\frac{\varkappa^2}{k^2}\cos^2(\varkappa r_0) = 1+\left(\frac{\varkappa^2}{k^2}-1\right)\cos^2(\varkappa r_0)$$

$$= 1+\frac{k_0^2}{k^2}\cos^2(\varkappa r_0),$$

$$B^2 = \frac{k^2}{k^2+k_0^2\cos^2(\varkappa r_0)}.$$

problem 5, solution

(problem 27, chapter 2, Sakurai)

$$\vec{j}(\vec{r},t) = -\frac{i\hbar}{2\mu}\left(\psi^*\vec{\nabla}\psi - (\vec{\nabla}\psi^*)\psi\right) = \frac{\hbar}{\mu}\,\mathrm{Im}\left(\psi^*\vec{\nabla}\psi\right)$$

For the hydrogen atom we have

$$\psi_{n\ell m}(\vec{r},t) = R_{n\ell}(r)\, Y_{\ell m}(\theta\,\phi)\, e^{-i\frac{E_n}{\hbar}t}.$$

$Y_{\ell m}(\theta\phi) = C_{\ell m}\, P_\ell^m(\cos\theta)\, e^{im\phi}$, where $C_{\ell m}$ is a real constant and $P_\ell^m(\cos\theta)$ is real. $R_{n\ell}(r)$ is real.

$$\vec{\nabla}\psi_{n\ell m}(\vec{r},t) = \hat{r}\left(\frac{\partial}{\partial r}R_{n\ell}(r)\right) C_{\ell m}\, P_\ell^m(\cos\theta)\, e^{im\phi}\, e^{-i\frac{E_n}{\hbar}t}$$
$$+\hat{\theta}\,\frac{1}{r}\, R_{n\ell}(r)\, C_{\ell m}\left(\frac{\partial}{\partial\theta}P_\ell^m(\cos\theta)\right) e^{im\phi}\, e^{-i\frac{E_n}{\hbar}t}$$
$$+\hat{\phi}\,\frac{1}{r\sin\theta}\, R_{n\ell}(r)\, C_{\ell m}\, P_\ell^m(\cos\theta)\left(\frac{\partial}{\partial\phi}e^{im\phi}\right) e^{-i\frac{E_n}{\hbar}t}.$$

All functions of r and θ in $\psi_{n\ell m}(\vec{r})$ and $\vec{\nabla}\psi_{n\ell m}(\vec{r})$ are real.

$$\mathrm{Im}(\psi^*\vec{\nabla}\psi) = \mathrm{Im}\left[\hat{\phi}\,\frac{1}{r\sin\theta}\left[R_{n\ell}(r)\, C_{\ell m}\, P_\ell^m(\cos\theta)\right]^2 e^{-im\phi}\left(\frac{\partial}{\partial\phi}e^{im\phi}\right)\right]$$

If $m=0$ $\vec{j}(\vec{r},t)=0$, so for the ground state $\vec{j}=0$.

If $m\neq 0$ then $\vec{j}(\vec{r},t) = \hat{\phi}\,\frac{1}{r\sin\theta}\left[R_{n\ell}(r)\, C_{\ell m}\, P_\ell^m(\cos\theta)\right]^2 m.$

For $m\neq 0$ $\vec{j}(\vec{r},t) = j(r,\theta)\,\hat{\phi}$.