# Computational aspects

ONB $\psi_{k\ell m} = R_{k\ell}(r)\, Y_\ell^m(\theta,\varphi)$

Independent of m b/c $\hat{L}_\pm \psi_{k\ell m} \propto R_{k\ell m}(r)\, Y_\ell^{m\pm 1}(\theta,\varphi)$.

Generally depend on $\ell$. For example, continuous $\psi_{k\ell m}$ can't depend on $(\theta,\varphi)$ at the origin or if $R(r)\to 0$ as $r\to 0$.

Only $Y_0^0$

Orthogonality

$$\int d^3x\, \psi^*_{k\ell m}\psi_{k'\ell'm'}$$

$$= \int dr\, r^2 R^*_{k\ell}(r) R_{k'\ell'}(r) \underbrace{\int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta\, d\theta \left[Y_\ell^m\right]^* Y_{\ell'}^{m'}}_{\delta_{\ell\ell'}\delta_{mm'}}$$

$$= \boxed{\int dr\, r^2 R^*_{k\ell}(r) R_{k'\ell}(r) = \delta_{kk'}} \quad \left(\text{Valid only for } \ell=\ell'\right)$$

General wave function

$$\Psi(\vec{r}) = \sum_{k\ell m} c_{k\ell m} R_{\ell m}(r)\, Y_\ell^m(\theta,\varphi)$$

$$c_{k\ell m} = \int d^3x\, \psi^*_{k\ell m}(\vec{r})\, \Psi(\vec{r})$$

$$= \int_0^\infty r^2 dr\, R^*_{k\ell}(r) \int_0^{2\pi} d\varphi \int_0^{\pi} \sin\theta\, d\theta \left[Y_\ell^m(\theta,\varphi)\right]^* \Psi(\vec{r})$$

For measurements of $\hat{L}^2$ and $\hat{L}_z$, only the angular part is relevant.

$$\text{Define } \Psi(\vec{r}) =: \sum_{\ell m} \underbrace{u_{\ell m}(r)}_{\sum_k c_{k\ell m} R_{k\ell}(r)} Y_\ell^m(\theta, \varphi)$$

(Marginalize)

$$\Pr_{L^2, L_z}(\ell, m) = \sum_k |c_{k\ell m}|^2 = \int_0^\infty r^2 dr\, |u_{\ell m}(r)|^2$$

$$\Pr_{L^2}(\ell) = \sum_{m=-\ell}^{+\ell} \Pr_{L^2, L_z}(\ell, m) = \sum_{km} |c_{k\ell m}|^2$$

$$= \sum_m \int r^2 dr\, |u_{\ell m}(r)|^2$$

$$\Pr_{L_z}(m) = \sum_{\ell \geq |m|} \Pr_{L^2, L_z}(\ell, m) = \sum_{k\ell} |c_{k\ell m}|^2$$

$$= \sum_\ell \int r^2 dr\, |u_{\ell m}(r)|^2$$

| $\ell$ | $m$ | | |
|---|---|---|---|
| 0 | 0 | | |
| 1 | 0 | 1 | |
| 2 | 0 | 1 | 2 |
| ⋮ | | | |

# Central Potentials

$$L^2 = L_j L_j = -\hbar^2 \epsilon_{jkl}\epsilon_{jmn} x_k \partial_l (x_m \partial_n)$$

$$= -\hbar^2 (\delta_{km}\delta_{ln} - \delta_{kn}\delta_{lm}) x_k \partial_l (x_m \partial_n)$$

$$= -\hbar^2 \left[ x_k \partial_l (x_k \partial_l) - x_k \partial_l (x_l \partial_k) \right]$$

$$= -\hbar^2 \left( \delta_{lk} x_k \partial_l + x_k x_k \partial_l \partial_l - 3 x_k \partial_k - x_k x_l \partial_l \partial_k \right)$$

$$= -\hbar^2 \left[ -2\vec{r}\cdot\vec{\nabla} + r^2 \nabla^2 - (\vec{r}\cdot\vec{\nabla})^2 \right]$$

$$= -\hbar^2 r^2 \nabla^2 + \hbar^2 \frac{\partial}{\partial r}\left( r^2 \frac{\partial}{\partial r} \right)$$

In the last line, we have used the fact that

$$\frac{\partial f}{\partial r} = \frac{\partial f}{\partial x}\frac{dx}{dr} + \frac{\partial f}{\partial y}\frac{dy}{dr} + \frac{\partial f}{\partial z}\frac{dz}{dr}$$

$$= \frac{\partial f}{\partial x}\sin\theta\cos\varphi + \frac{\partial f}{\partial y}\sin\theta\sin\varphi + \frac{\partial f}{\partial z}\cos\theta$$

$$= \hat{r}\cdot\vec{\nabla} f$$

$$\Rightarrow r\frac{\partial f}{\partial r} = r\hat{r}\cdot\vec{\nabla} f = \vec{r}\cdot\vec{\nabla} f \Rightarrow r\frac{\partial}{\partial r} = \vec{r}\cdot\vec{\nabla}$$

It follows that $\left(r\frac{\partial}{\partial r}\right)^2 + 2r\frac{\partial}{\partial r} = \frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)$

In particular, $\boxed{L^2 = r^2p^2 + \hbar^2 \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)}$

Substitute this into the kinetic energy operator gives

$$\boxed{\hat{T} = \frac{\hat{p}^2}{2m} = \frac{\hat{L}^2}{2mr^2} - \frac{\hbar^2}{2mr^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)}$$

For a spherically symmetric potential $V = V(r)$

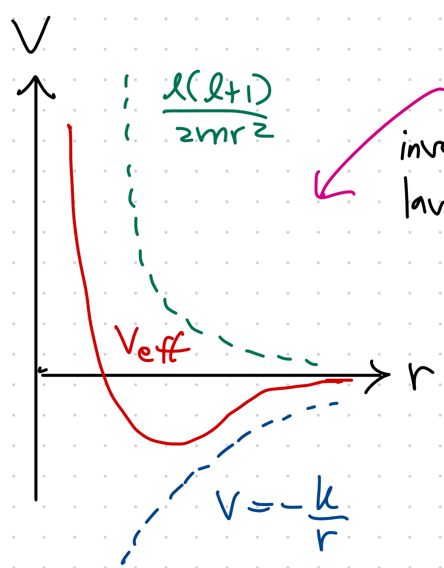
$[\hat{H}, \hat{L}] = 0$. Consequently, stationary states are of the form

$$\varphi_{E\ell m}(\vec{r}) = R_{E\ell}(r)\, Y_\ell{}^m(\theta, \varphi)$$

TISE

$$\left[\frac{-\hbar^2}{2mr^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) + \underbrace{\overbrace{\frac{\ell(\ell+1)\hbar^2}{2mr^2}}^{\text{Centrifugal potential}} + V(r)}_{V_{eff}(r)}\right] R_{E\ell} = E R_{E\ell}$$

Effective potential




inverse-square-law force & $\ell \neq 0$

Trick Change of Function $R_{kl}(r) = \frac{u_{kl}(r)}{r}$

$$\frac{1}{r^2}\frac{d}{dr}\left[r^2\frac{d}{dr}\left(\frac{u}{r}\right)\right] = \frac{1}{r^2}\frac{d}{dr}\left(r\frac{du}{dr} - u\right)$$

$$= \frac{1}{r^2}\left(\cancel{\frac{du}{dr}} + r\frac{d^2u}{dr^2} - \cancel{\frac{du}{dr}}\right) = \frac{1}{r}\frac{d^2}{dr^2}$$

$\therefore$ We have that

$$\underbrace{\frac{-\hbar^2}{2mr^2}\frac{d}{dr}\left[r^2\frac{d}{dr}\left(\frac{u}{r}\right)\right]}_{-\frac{\hbar^2}{2m}\frac{u''}{r}} + \frac{\hbar^2}{2mr^2}l(l+1)\frac{u}{r} + V(r)\frac{u}{r} = E\frac{u}{r}$$

Multiply both sides by $r$;

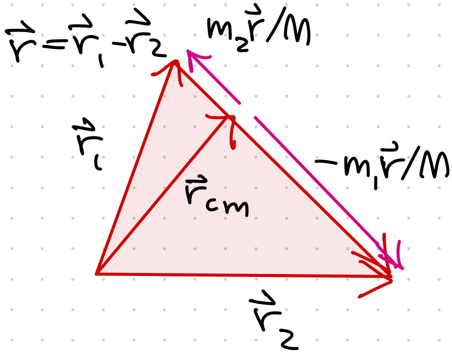
$$-\frac{\hbar^2}{2m}u'' + \frac{\hbar^2}{2mr^2}l(l+1)u + V(r)u = Eu$$

$$\boxed{\left[\frac{d^2}{dr^2} + \frac{2m\left(E_{kl} - V_{eff}(r)\right)}{\hbar^2}\right]u_{kl}(r) = 0}$$

Precisely the same mathematical form as the TISE in 1D!

Two interacting particles

$$H = \frac{\vec{p}_1^{\,2}}{2m_1} + \frac{\vec{p}_2^{\,2}}{2m_2} + V(\vec{r}_1 - \vec{r}_2)$$




$$M = m_1 + m_2$$

$$\vec{r}_{cm} = \frac{m_1\vec{r}_1 + m_2\vec{r}_2}{M}, \qquad \vec{r} = \vec{r}_1 - \vec{r}_2$$

$$\vec{r}_1 = \vec{r}_{cm} + \frac{m_2}{M}\vec{r}$$

$$\vec{r}_2 = \vec{r}_{cm} - \frac{m_1}{M}\vec{r}$$

If we take $\vec{r}_{cm}$ as the origin, then $m_1\tilde{\vec{r}}_1 + m_2\tilde{\vec{r}}_2 = 0$

Scale factor

and $\tilde{\vec{r}} = \tilde{\vec{r}}_1 - \tilde{\vec{r}}_2 = \tilde{\vec{r}}_1 + \frac{m_1}{m_2}\tilde{\vec{r}}_1 = \frac{M}{m_2}\tilde{\vec{r}}_1 = \frac{m_1}{\mu}\tilde{\vec{r}}_1$

The inverse of the pre-factor is the reduced mass $\mu < m_1, m_2$

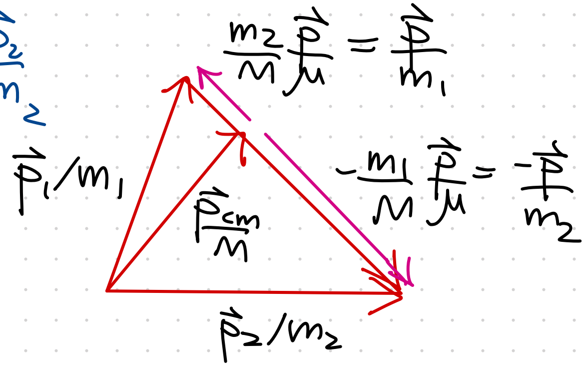
$$\boxed{\mu = \frac{m_1 m_2}{m_1 + m_2}, \qquad \frac{1}{\mu} = \frac{1}{m_1} + \frac{1}{m_2}}$$

(Relative velocity)

$$\vec{p}_{cm} = \vec{p}_1 + \vec{p}_2, \qquad \frac{\vec{p}}{\mu} = \frac{\vec{p}_1}{m_1} - \frac{\vec{p}_2}{m_2}$$

$$\vec{p}_1 = \vec{p} + \frac{m_1}{M}\vec{p}_{cm}$$

$$\vec{p}_2 = -\vec{p} + \frac{m_2}{M}\vec{p}_{cm}$$



$$\frac{\vec{p}_{cm}}{M} = \frac{\vec{p}_1}{M} + \frac{\vec{p}_2}{M} = \frac{\vec{p}_1}{m_1}\frac{m_1}{M} + \left(\frac{\vec{p}_1}{m_1} - \frac{\vec{p}}{\mu}\right)\frac{m_2}{M}$$

$$= \frac{\vec{p}_1}{m_1} - \vec{p}\,\frac{\cancel{M}}{m_1 \cancel{m_2}}\,\frac{\cancel{m_2}}{\cancel{M}} \Rightarrow \frac{m_1}{M}\vec{p}_{cm} = \vec{p}_1 - \vec{p}$$

Commutation relation → A question of an efficient notation

$$[R_{cm}, R] = 0, \quad [P_{cm}, P] = 0$$

$$[R_{cm}, P_{cm}] = \left[\frac{m_1}{M}R_1 + \frac{m_2}{M}R_2, P_1 + P_2\right]$$

$$= i\hbar\left(\cancel{\frac{m_1}{M} + \frac{m_2}{M}}\right) = i\hbar$$

$$[R_{cm}, P] = \left[\frac{m_1}{M}R_1 + \frac{m_2}{M}R_2, \frac{\mu}{m_1}P_1 - \frac{\mu}{m_2}P_2\right]$$

$$= \frac{\mu}{M}\left([R_1, P_1] - [R_2, P_2]\right) = 0$$

$$[R, P_{cm}] = [R_1 - R_2, P_1 + P_2] = 0$$

$$[R, P] = \left[R_1 - R_2, \frac{\mu}{m_1}P_1 - \frac{\mu}{m_2}P_2\right]$$

$$= i\hbar\left(\cancel{\frac{\mu}{m_1} + \frac{\mu}{m_2}}\right) = i\hbar$$

⇒ Independent Hilbert spaces $\mathcal{H}_{cm} \otimes \mathcal{H}_{relative}$

$$L = L_1 + L_2 = R_1 \times P_1 + R_2 \times P_2$$

$$= \left(R_{cm} + \frac{m_1}{M} R\right) \times \left(P + \frac{m_1}{M} P_{cm}\right)$$

$$+ \left(R_{cm} - \frac{m_1}{M} R\right) \times \left(-P + \frac{m_2}{M} P_{cm}\right)$$

$$= \cancel{R_{cm} \times P} + \frac{m_1}{M} R_{cm} \times P_{cm} + \frac{m_2}{M} R \times P + \cancel{\frac{m_1 m_2}{M^2} R \times P_{cm}}$$

$$\cancel{- R_{cm} \times P} + \frac{m_2}{M} R_{cm} \times P_{cm} + \frac{m_1}{M} R \times P \cancel{- \frac{m_1 m_2}{M^2} R \times P_{cm}}$$

$$= \boxed{R_{cm} \times P_{cm} + R \times P}$$

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Back to $\hat{T} = \frac{p_1^2}{2m_1} + \frac{p_2^2}{2m_2} = \frac{1}{2m_1}\left(p + \frac{m_1}{M} p_{cm}\right)^2$

$$+ \frac{1}{2m_2}\left(-p + \frac{m_2}{M} p_{cm}\right)^2$$

$$= \frac{p^2}{2\mu} + \frac{p_{cm}^2}{2M}$$

In the CM frame, $m_1 \vec{r}_1 + m_2 \vec{r}_2 = 0$

$$\Rightarrow m_1 \dot{\vec{r}}_1 + m_2 \dot{\vec{r}}_2 = \vec{p}_1 + \vec{p}_2 = \vec{p}_{cm} = 0$$

$$\Rightarrow \hat{T} = \frac{p^2}{2\mu} = \frac{\hat{L}^2}{2\mu r^2} - \frac{\hbar^2}{2\mu r^2} \frac{\partial}{\partial r}\left(r^2 \frac{\partial}{\partial r}\right)$$

i.e. simply replace $m$ with the reduced mass $\mu$.

Ex Hydrogen atom $V(r) = \frac{q_p q_e}{r} = -\frac{e^2}{r}$

Proton charge $q_p = e$, $m_p \approx 1.7 \times 10^{-27}$ kg

Electron charge $q_e = -e$, $m_e \approx 0.91 \times 10^{-30}$ kg

$$\mu = \frac{m_e m_p}{m_e + m_p} = m_e \left(1 + \frac{m_e}{m_p}\right)^{-1}$$

$$\approx m_e \left(1 - \frac{m_e}{m_p}\right)$$

Generalize $(1+\epsilon)^n = 1 + n\epsilon + \frac{n(n-1)}{2}\epsilon^2 + \mathcal{O}(n^3)$ to negative powers

$m_e/m_p \sim 1/1800$. Excellent approximation to treat the proton as an unmoving center of mass.

B.C. at $r=0$

Merzbacher p.263 –

① $\ell \geq 1$: $R_{k\ell}(r) \underset{r\to 0}{\sim} C r^s$

Assume centrifugal force dominates near $r=0$

$$\frac{d^2u}{dr} - \frac{\ell(\ell+1)}{r^2}u = 0 \Rightarrow \text{Two solutions } \begin{cases} s=\ell \\ s=-(\ell+1) \end{cases}$$

$$u = Ar^{\ell+1} + \boxed{Br^{-\ell}} \leftarrow \text{Blow up at } r=0$$

Pick $s=\ell \Rightarrow u_{k\ell}(0)=0$

② $\ell=0$; $u(0)=0$ by requiring $\hat{H}$ to be Hermitian.

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B.C. at $r=\infty$. Assume $V \underset{r\to\infty}{\to} 0$

Bound state $E_{k\ell}<0$ $\quad \frac{d^2u_{k\ell}}{dr^2} + \frac{2\mu E_{k\ell}}{\hbar^2}u_{k\ell} = 0$

$$u_{k\ell}(r) \sim \exp\Big(-\underbrace{\sqrt{\frac{-2\mu E_{k\ell}}{\hbar}}}_{\kappa}\, r\Big)$$

Define $\rho = \kappa r$

$$u(r) = \underbrace{\rho^{\ell+1}}_{\text{sol. near } r=0}\ \underbrace{e^{-\rho}}_{\text{sol. at } r\to\infty}\ \underbrace{w(\rho)}_{\text{Assume series solution}} \qquad w(\rho) = a_0 + a_1\rho + a_2\rho^2 + \cdots$$

$$\frac{d^2w}{d\rho^2} + 2\left(\frac{\ell+1}{\rho} - 1\right)\frac{dw}{d\rho} + \left[\frac{V}{E} - \frac{2(\ell+1)}{\rho}\right]w = 0$$