8.322: Quantum Theory II

Problem Set #6 Solutions
April 9, 2007

1. **Reflection above the barrier**

(a)

We begin with the formula for scattering above a barrier from the notes,

$$|R|^2 = \exp\left(\frac{-2}{\hbar}\int_{-p_0(E)}^{p_0(E)} dp \mathrm{Im}\left[V^{-1}(E - \frac{p^2}{2m})\right]\right)$$

Here $V(x) = -V_0\sqrt{1 + x^2/a^2}$, thus

$$y = -V_0\sqrt{1 + \frac{x^2}{a^2}} \Longrightarrow x = a\sqrt{\frac{y^2}{V_0^2} - 1}$$

which gives

$$V^{-1}(y) = a\sqrt{\frac{y^2}{V_0^2} - 1}.$$

Here $E = 0$ and plugging in for V^{-1} and p_0 into the expression for $|R|^2$ gives

$$\begin{aligned}
|R|^2 &= \exp\left(\frac{-4}{\hbar}\int_0^{\sqrt{2mV_0}} dpa\sqrt{1 - \frac{p^4}{4m^2V_0^2}}\right) \\
&= \exp\left(-4\sqrt{\frac{2ma^2V_0}{\hbar^2}}\int_0^1 dpa\sqrt{1 - p^4}\right) \\
&= \exp\left(-4\sqrt{\frac{2ma^2V_0}{\hbar^2}}\frac{\sqrt{\pi}\Gamma(\frac{1}{4})}{8\Gamma(\frac{7}{4})}\right) \\
&= \exp\left(-\frac{\sqrt{2\pi}\Gamma(\frac{1}{4})}{2\Gamma(\frac{7}{4})}\sqrt{\frac{mV_0a^2}{\hbar^2}}\right)
\end{aligned}$$

(b)

Using the results derived from the notes with the proper modifications we find

$$|R|^2 = \exp\left(-2\pi\sqrt{\frac{mV_0a^2}{\hbar^2}}\right)$$

We see that the results in (a) and (b) have the same dependence on strength and width of the barrier, but the numerical prefactor is different. In particular the inverted oscillator underestimates the WKB reflection probability for the potential considered in part (a).

2. **A slow field reversal**

(a) Adiabatic evolution requires

$$T \gg \frac{\hbar}{\Delta E}$$

where T is the time scale of the change and ΔE is the energy difference between the eigenstates. If the field is slowly reversed, then at some point the B–field goes to zero and the two spin states become degenerate. If the states become degenerate it is no longer possible to prevent a transition since the adiabatic approximation fails. By rotating the magnetic field, we can keep ΔE at a constant $\mu_e B$ value and avoid the level degeneracy that causes the approximation to fail.

(b) The xy–plane field ensures that the magnetic field never vanishes and therefore no degeneracy appears (see Figure 1).

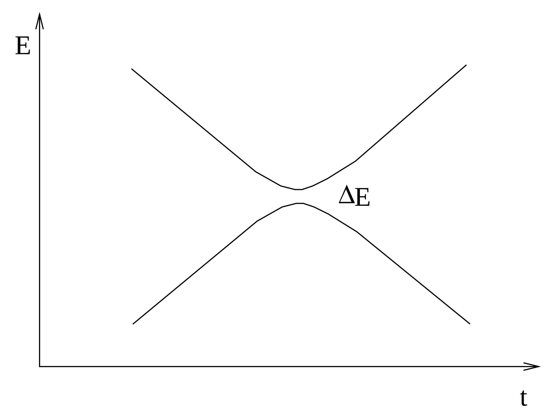

Figure 1: By turning on a permanent B_0 magnetic field, we obtain $\Delta E_{min} = \mu_e B_0 > 0$

Hence, the electron spin can be reversed as long as the magnetic field changes slowly.

(c) Let us assume that B_z is changed linearly from B_{z0} to $B(T) = -B_{z0}$. The Hamiltonian is

$$\frac{\mu_e}{2}\begin{pmatrix} B_z(t) & B_x \\ B_x & -B_z(t) \end{pmatrix}$$

where $B_z(t) = \frac{2B_z^0 t}{T}$, where t goes from $-T/2$ to $T/2$. This is the same setup that was discussed in the supplementary notes with the following identifications

$$\epsilon \equiv \frac{1}{2}\mu_e B_x \qquad f(t) \equiv \frac{\mu_e B_z^0 t}{T}$$

Hence, the probability of flipping is

$$|R|^2 = \exp\left(-\pi T \mu_e \frac{B_x^2}{4\hbar B_z^0}\right) \leq 10^{-6}.$$

We plug in

$$B_z^0 = 5 \text{ kG} = 1000\ B_x$$

and

$$\mu_e \approx 2\mu_B = \frac{e\hbar}{m_e}$$

and obtain

$$10^{-6} \geq \exp\left(-\frac{e\pi B_x T}{4000\ m_e}\right)$$

and thus

$$T \geq -\ln(10^{-6})\frac{4000\ m_e}{e\pi B_0} = 200\ \mu s$$

3. **Quantum Adiabatic Engineering**

(a) After subtracting the total energy, the Hamiltonian is

$$H = -\mu_0 \frac{1}{\hbar}\vec{S}\cdot\vec{B} - c\frac{1}{\hbar^2}S_z^2 = \begin{pmatrix} -c-\mu_0(B_0-\beta t) & -\mu_0 B_x & 0 \\ -\mu_0 B_x & 0 & -\mu_0 B_x \\ 0 & -\mu_0 B_x & -c+\mu_0(B_0-\beta t) \end{pmatrix}$$

For $t = 0$

$$H \approx \begin{pmatrix} -c-\mu_0 B_0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & -c+\mu_0 B_0 \end{pmatrix}$$

with eigenvalues

$$E = 0, \quad -c \pm \mu_0 B_0$$

For $t = \frac{1}{\beta}(B_0 - c/\mu_0)$

$$H \approx \begin{pmatrix} -2c & -\mu_0 B_x & 0 \\ -\mu_0 B_x & 0 & -\mu_0 B_x \\ 0 & -\mu_0 B_x & 0 \end{pmatrix}$$

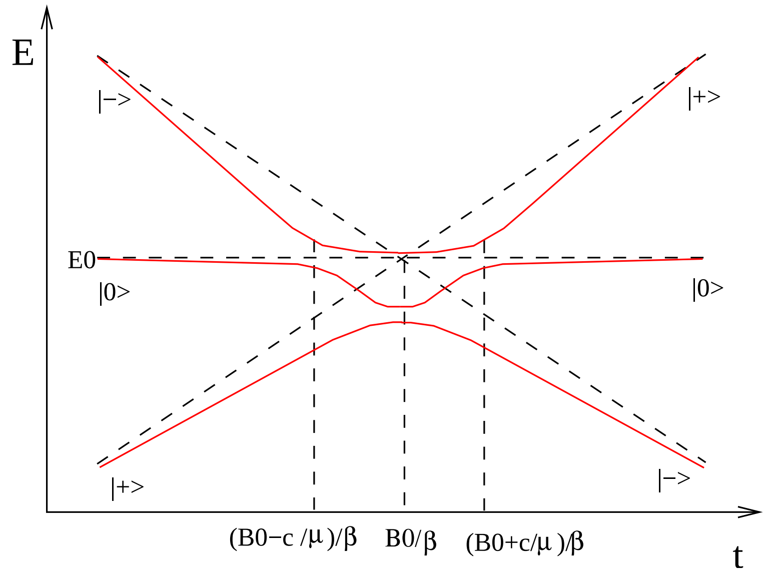

Figure 2: Energy levels.

with eigenvalues

$$E \approx -2c, \quad \pm\mu_0 B_x$$

For $t = \frac{B_0}{\beta}$

$$H \approx \begin{pmatrix} -c & -\mu_0 B_x & 0 \\ -\mu_0 B_x & 0 & -\mu_0 B_x \\ 0 & -\mu_0 B_x & -c \end{pmatrix}$$

with eigenvalues

$$E \approx -c, \quad -c - \frac{2}{c}\mu_0^2 B_x^2, \quad \frac{2}{c}\mu_0^2 B_x^2$$

Note that the eigenvector with the largest eigenvalue is mostly $\sim \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix}$.

Figure 2 shows the sketch of energy levels.

(b) As we have already shown in (a), by $t = \frac{B_0}{\beta}$ the $|-\rangle$ state has adiabatically evolved to $|0\rangle$ (see Figure 2). If we let it adiabatically evolve for another $t = \frac{B_0}{\beta}$, then it will be in the $|+\rangle$ state.

If we want to end up in the state $|0\rangle$, we adiabatically evolve for a time $t \approx \frac{B_0}{\beta}$ which brings us to a state close to $|0\rangle$. Then we do not allow the field to change further.

4. **Simplifying Degeneracies in the Adiabatic Approximation**

The Hamiltonian is

$$H = \begin{pmatrix} E_0 + \sum_{j=1}^{N} \langle a_1 | \delta\alpha_j \left. \frac{\partial H}{\partial \alpha_j} \right|_{\alpha^0} | a_1 \rangle & \sum_{j=1}^{N} \langle a_1 | \delta\alpha_j \left. \frac{\partial H}{\partial \alpha_j} \right|_{\alpha^0} | a_2 \rangle \\ \sum_{j=1}^{N} \langle a_2 | \delta\alpha_j \left. \frac{\partial H}{\partial \alpha_j} \right|_{\alpha^0} | a_1 \rangle & E_0 + \sum_{j=1}^{N} \langle a_2 | \delta\alpha_j \left. \frac{\partial H}{\partial \alpha_j} \right|_{\alpha^0} | a_2 \rangle \end{pmatrix}$$

The trace of the Hamiltonian tells us the average energy which is of no importance in this problem. Therefore we consider the traceless

$$H' = H - \frac{1}{2}\mathrm{Tr}H$$

Since H' is a 2×2 traceless Hermitian matrix, it can be written as a linear combination of the Pauli matrices

$$H' = \sum_k B_k \sigma^k$$

Using $\mathrm{Tr}(\sigma^i \sigma^j) = 2\delta_{ij}$,

$$\mathrm{Tr}(\sigma^i H') = \mathrm{Tr}\left(\sum_k B_k \sigma^i \sigma^k\right) = \sum_k \mathrm{Tr}(B_k \sigma^i \sigma^k) = 2B_i$$

Hence,

$$B_k = \frac{1}{2}\mathrm{Tr}(\sigma^k H') = \frac{1}{2}\sum_{m,n=1,2} \sigma^k_{mn} H'_{nm} = \frac{1}{2}\sum_{m,n=1,2} \sigma^k_{mn} H_{nm}$$

And thus

$$B_k = \frac{1}{2}\sum_{m,n=1,2} \sigma^k_{mn} \langle a_m | \delta\alpha_j \left. \frac{\partial H}{\partial \alpha_j} \right|_{\alpha^0} | a_n \rangle.$$

5. **Berry Phase for Spin-J**

The Berry phase is given by

$$\gamma_{M_J}(C) = -\mathrm{Im}\left\{ \sum_{m \neq M_J} \int_S d\vec{S}\ \frac{\langle J, M_J | \nabla_B \vec{S} \cdot \vec{B} | J, m \rangle \times \langle J, m | \nabla_B \vec{S} \cdot \vec{B} | J, M_J \rangle}{(M_J - m)^2 |\vec{B}|^2} \right\}$$

$$\gamma_{M_J}(C) = -\mathrm{Im}\left\{ \sum_{m \neq M_J} \int_S d\vec{S}\ \frac{\langle J, M_J | \vec{S} | J, m \rangle \times \langle J, m | \vec{S} | J, M_J \rangle}{(M_J - m)^2 |\vec{B}|^2} \right\} \qquad (0.1)$$

The spin operators give the followings

$$S_x | J, m \rangle = \frac{1}{2}(S_+ + S_-) | J, m \rangle = \frac{1}{2}\sqrt{(J-m)(J+m+1)} | J, m+1 \rangle + \frac{1}{2}\sqrt{(J+m)(J-m+1)} | J, m-1 \rangle$$

$$S_y | J, m \rangle = \frac{1}{2i}(S_+ - S_-) | J, m \rangle$$

Only $m = M_J \pm 1$ contributes to the sum.

$$S_z|J,m\rangle = m|J,m\rangle$$

The x, y components of $\langle J, M_J|\vec{S}|J,m\rangle \times \langle J,m|\vec{S}|J,M_J\rangle$ are zero since $\langle J, M_J|\vec{S}_z|J,m\rangle = 0$. Hence, by substituting the above expressions into (0.1), we obtain

$$\gamma_{M_J}(C) = -\text{Im}\left\{\int_S d\vec{S}\frac{\hat{B}}{|\vec{B}|^2}\left(\frac{1}{2i}(J+M_J+1)(J-M_J) - \frac{1}{2i}(J-M_J+1)(J+M_J)\right)\right\}$$

$$\gamma_{M_J}(C) = \frac{1}{2}\int_S d\vec{S}\frac{\hat{B}}{|\vec{B}|^2}(-2M_J) = -M_J\Omega(C)$$

6. **An adiabatic excursion**

(a) The criterion for the adiabatic approximation is

$$\frac{\hbar}{|\Delta E(t)|^2}\left[\frac{d}{dt}\Delta E(t)\right] \ll 1$$

Here

$$\left[\frac{d}{dt}\Delta E(t)\right] \approx \frac{e\hbar\omega B}{mc}$$

and

$$\Delta E(t) \approx \frac{e\hbar B_0}{mc} = \hbar\omega_L$$

Thus

$$\frac{\omega e B}{mc} \ll \omega_L^2 \Longrightarrow \frac{\omega}{\omega_L} \ll \frac{B_0}{B}$$

(b) The Hamiltonian for the two state system is given by

$$\begin{aligned} H(t) &= -\frac{ge}{2mc}\frac{\hbar}{2}\vec{\sigma}\cdot\vec{B} \\ &= -\frac{e\hbar}{2mc}\begin{pmatrix} B_0 & B(\cos\lambda\cos\omega t - i\sin\lambda\sin\omega t) \\ B(\cos\lambda\cos\omega t + i\sin\lambda\sin\omega t) & -B_0 \end{pmatrix} \end{aligned}$$

This has eigenvalues

$$E_\pm = \pm\frac{e\hbar}{2mc}\sqrt{B_0^2 + B^2\cos^2\lambda\cos^2\omega t + B^2\sin^2\lambda\sin^2\omega t}$$

The energy difference between the two levels is a minimum at $t = \frac{(2n+1)\pi}{2\omega}$, since $0 < \lambda < \frac{\pi}{4}$. Expanding about the minimum, let $B_m = \sqrt{B_0^2 + B^2\sin^2\lambda}$

$$\begin{aligned} \Delta E(\Delta t) &= \frac{e\hbar}{mc}\left(B_m + \frac{B^2\omega^2}{2B_m}(\cos^2\lambda - \sin^2\lambda)\Delta t^2 + \dots\right) \\ &\equiv \sqrt{\epsilon^2 + \Delta t^2/T^2}. \end{aligned}$$

where

$$\epsilon^2 = \left(\frac{e\hbar B_m}{mc}\right)^2$$

$$\frac{1}{T} = \frac{e\hbar}{mc} B\omega\sqrt{\cos^2\lambda - \sin^2\lambda}$$

Thus using the results from the notes

$$\begin{aligned}
|R|^2 &= \exp\left(-\pi T\epsilon^2/\hbar\right) \\
&= \exp\left(-\pi\frac{e}{mc}\frac{B_m^2}{B\omega\sqrt{\cos^2\lambda - \sin^2\lambda}}\right) \\
&\approx \exp\left(-\pi\frac{B_0\omega_L}{B\omega}\frac{1 + \frac{B^2}{2B_0^2}\sin^2\lambda}{\sqrt{\cos^2\lambda - \sin^2\lambda}}\right)
\end{aligned}$$

Thus the transition probability per unit time is approximately

$$\frac{\pi}{\omega}|R|^2$$

with $|R|^2$ given as above.

(c) We begin with

$$\Delta E(t) \approx \frac{e\hbar B_0}{mc}\left(1 + \frac{B^2}{2B_0^2}(\cos^2\lambda\cos^2\omega t + \sin^2\lambda\sin^2\omega t\right)$$

Ignoring the adiabatic phase the we have the condition

$$\int_0^T \Delta E(t)dt = 2\pi\hbar$$

which gives to order B^2/B_0^2

$$\frac{2\pi}{\omega_L} = T + \frac{B^2}{4B_0^2}\left(T + \frac{\cos 2\lambda\sin 2T\omega}{2\omega}\right) + \ldots$$

Solving for T to order B^2/B_0^2 gives

$$T = \frac{2\pi}{\omega_L}\left[1 - \frac{B^2}{4B_0^2}\left(1 + \frac{\omega_L}{4\pi\omega}\cos 2\lambda\sin\frac{4\pi\omega}{\omega_L}\right)\right]$$

where $\omega_L = eB_0/mc$.

(d) Due to the Berry's phase there will be an extra phase difference Ω, where Ω is the solid angle traced out by $\vec{B}$. Since $B_0 \gg B$ we assume that we can calculate the solid angle by taking the area of the ellipse traced out and using $R = B_0$ ignoring the curvature. Thus

$$\Omega = \pi \frac{B^2}{2B_0^2} \sin 2\lambda$$

This changes (c) such that

$$2\pi\hbar = \int_0^T \Delta E(t)dt + \frac{\hbar\Omega\omega}{2\pi} T$$

$$\frac{2\pi}{\omega_L} = \tilde{T} + \frac{B^2}{4B_0^2}\left(\tilde{T} + \frac{\cos 2\lambda \sin 2\tilde{T}\omega}{2\omega}\right) + \tilde{T}\frac{B^2}{4B_0^2}\frac{\omega}{\omega_L}\sin 2\lambda$$

Thus

$$\tilde{T} - T = -\frac{\pi\omega B^2}{2\omega_L^2 B_0^2}\sin 2\lambda$$

7. **Bohm-Aharonov Effect**

The $\psi_n(\vec{r}, \vec{R})$ eigenstate satisfies the Schrödinger equation

$$\left(\frac{1}{2m}\left(\frac{\hbar\vec{\nabla}_r}{i} - \frac{e}{c}\vec{A}(\vec{r})\right)^2 + V(\vec{r} - \vec{R})\right)\psi_n(\vec{r}, \vec{R}) = E_n(\vec{R})\ \psi_n(\vec{r}, \vec{R})$$

We can eliminate the vector potential from the Schrödinger equation by making a phase transformation of the wavefunction. Since ψ_n is localized in a region where the B–field vanishes, we can define

$$\psi_n(\vec{r}, \vec{R}) = e^{ig(\vec{r},\vec{R})}\phi_n(\vec{r} - \vec{R})$$

where

$$g(\vec{r}, \vec{R}) = \frac{e}{\hbar c}\int_{\vec{R}}^{\vec{r}} \vec{A}(\vec{x}) \cdot d\vec{x}$$

Substituting this back into the Schrödinger equation gives

$$\left(\frac{1}{2m}\left(\frac{\hbar\vec{\nabla}_r}{i}\right)^2 + V(\vec{r} - \vec{R})\right)\phi_n(\vec{r} - \vec{R}) = E_n(\vec{R})\ \phi_n(\vec{r} - \vec{R})$$

that is ϕ_n is the n–th eigenfunction in the localized potential in the absence of B–field.

The Berry phase is given by

$$\gamma_n(C) = i\oint_C \langle\psi_n|\vec{\nabla}_R|\psi_n\rangle \cdot d\vec{R}$$

$$\nabla_R \psi_n = \nabla_R \left(e^{ig(\vec{r},\vec{R})} \phi_n(\vec{r}-\vec{R}) \right) = \left(-\frac{ie}{\hbar c} A(\vec{R}) \phi_n(\vec{r}-\vec{R}) - \vec{\nabla}_r \phi_n(\vec{r}-\vec{R}) \right) e^{ig(\vec{r},\vec{R})}$$

Therefore

$$\gamma_n(C) = \frac{e}{\hbar c} \oint_C A(\vec{R}) \cdot d\vec{R} + \oint_C \left(\int \phi_n^*(\vec{r}-\vec{R})(-i\vec{\nabla}_r)\phi_n(\vec{r}-\vec{R})\ d^3\vec{r} \right) \cdot d\vec{R}$$

$$\gamma_n(C) = \frac{e}{\hbar c} \iint_S \vec{B} \cdot d\vec{R} + \underbrace{\oint_C \frac{1}{\hbar} \langle \phi_n | \vec{p} | \phi_n \rangle \cdot d\vec{R}}_{0,\ \text{because } \phi_n \text{ is a stationary state}}$$

$$\gamma_n(C) = \frac{e}{\hbar c} \Phi_B$$

8. **Hannay's Angle**

(a) The only difference between the two problems is that in the case of the helix the wheel center of mass moves in a vertical direction. The axis of the wheel executes the same cone. One can achieve this by applying a constraint force which exerts no additional torque on the wheel. Hence the two problems are equivalent.

(b) The equation of the helix is

$$\vec{r}(s) = \hat{x}\cos(\alpha)\cos(s) + \hat{y}\cos(\alpha)\sin(s) + \hat{z}s\sin(\alpha)$$

By definition

$$\hat{n}(s) = \frac{\dot{\hat{t}}(s)}{|\dot{\hat{t}}(s)|} = \frac{-\hat{x}\cos(\alpha)\cos(s) - \hat{y}\cos(\alpha)\sin(s)}{\sqrt{\cos^2(\alpha)}} = -\hat{x}\cos(s) - \hat{y}\sin(s)$$

$$\hat{b}(s) = \hat{t}(s) \times \hat{n}(s) = \hat{x}\sin(\alpha)\sin(s) - \hat{y}\sin(\alpha)\cos(s) + \hat{z}\cos(\alpha)$$

(c) Since $\dot{\hat{t}}(s) = |\dot{\hat{t}}(s)|\ \hat{n}(s)$, we obtain $\kappa(s) = |\dot{\hat{t}}(s)| = \cos(\alpha)$.

Now,

$$\frac{d\hat{n}}{ds} = \hat{x}\sin(s) - \hat{y}\cos(s) = \hat{x}(\sin(s)\cos^2(\alpha) + \sin(s)\sin^2(\alpha)) - \hat{y}(\cos^2(\alpha)\cos(s) + \sin^2(\alpha)\cos(s)) +$$

$$+\hat{z}(\cos(\alpha)\sin(\alpha) - \cos(\alpha)\sin(\alpha)) = -\cos(\alpha)\hat{t} + \sin(\alpha)\hat{b}$$

Hence,

$$\tau(s) = \sin(\alpha)$$

$$\frac{d\hat{b}}{ds} = \hat{x}\sin(\alpha)\cos(s) + \hat{y}\sin(\alpha)\sin(s) = -\sin(\alpha)\left(-\hat{x}\cos(s) - \hat{y}\sin(s)\right) = -\sin(\alpha)\hat{n}(s) = -\tau(s)\hat{n}(s)$$

(d) For any s, $\{\hat{t}(s), \hat{n}(s), \hat{b}(s)\}$ forms an orthonormal frame. In this frame, we can expand any $\vec{u}$ vector as

$$\vec{u} = u_t\hat{t} + u_n\hat{n} + u_b\hat{b}$$

In particular,

$$\vec{\omega}_{Frenet} = \omega_t\hat{t} + \omega_n\hat{n} + \omega_b\hat{b}$$

By plugging this into $\dot{\vec{u}} = \vec{\omega}_{Frenet} \times \vec{u}$, we obtain

$$\dot{\hat{t}}(s) = -\omega_n\hat{b} + \omega_b\hat{n}$$

$$\dot{\hat{n}}(s) = \omega_t\hat{b} - \omega_b\hat{t}$$

$$\dot{\hat{b}}(s) = -\omega_t\hat{n} + \omega_n\hat{b}$$

Comparing this to the Frenet formula gives

$$\omega_t = \tau(s) \qquad \omega_n = 0 \qquad \omega_b = \kappa(s)$$

Hence,

$$\vec{\omega}_{Frenet} = \tau(s)\hat{t} + \kappa(s)\hat{b} = \hat{z}$$

We have

$$\hat{t} \cdot \vec{\omega}_{Frenet} = \omega_t = \tau(s) = \sin(\alpha)$$

which is not always zero. Thus, the orange spoke will move in the Frenet frame.

(e) We define

$$\vec{v}(s) = \cos\theta(s)\ \hat{n}(s) + \sin\theta(s)\ \hat{b}(s)$$

Now

$$\frac{d\vec{v}}{ds} = \left(\cos\theta\ \dot{\hat{n}} + \sin\theta\ \dot{\hat{b}}\right) + \dot{\theta}\left(-\sin\theta\ \dot{\hat{n}} + \cos\theta\ \dot{\hat{b}}\right)$$

$$= -\kappa(s)\cos\theta\hat{t} - \left(\tau(s)\sin\theta + \sin\theta\dot{\theta}\right)\hat{n} + \left(\tau(s)\cos\theta + \dot{\theta}\cos\theta\right)\hat{b}$$

We also know that

$$\frac{d\vec{v}}{ds} = \vec{\omega}_{Frenet} \times \vec{v} = \omega_n \sin\theta\hat{t} - \omega_b\cos\theta\hat{t}$$

Matching the components, we have

$$\frac{d\theta}{ds} = -\tau(s)$$

(f)

$$\Delta\theta = \theta(2\pi) - \theta(0) = \int_0^{2\pi} \frac{d\theta}{ds} ds = -2\pi\sin\alpha = \Omega$$

From (a) we know that taking s from 0 to 2π is equivalent to having the wheel on the rod execute a conical motion. (Then, $\Delta\theta$ measures the change in the angle of the orange spoke after one revolution.) This cone is analogous to the cone traced by the parameter $\vec{R}$ during adiabatic motion in quantum mechanics. $\Delta\theta$ is the solid angle subtended by the rod during one cycle.

(g) All the steps in the derivation are unchanged except for the explicit formulas for the curvature and torsion in terms of the angle α. In particular, the equation $d\theta/ds = -\tau(s)$ is valid in general. Also the solid angle swept out by the cone is $\int \tau(s)ds$ over a closed curve. Thus the result is preserved and the generalization gives

$$\Delta\theta = \Omega$$

where Ω is now the solid angle subtended by the surface whose boundary cycle is swept through by the axis of the wheel.

9. **The Born-Oppenheimer Approximation for a Diatomic Molecule**

(a)

$$H = -\frac{1}{2M_N}\nabla_R^2 - \frac{1}{2m_e}\nabla_r^2 + V_N(\vec{R}) + V_e(\vec{r},\vec{R})$$

$$\Psi(\vec{r},\vec{R}) = \sum_m \Phi_m(\vec{R})\psi_m(\vec{r},\vec{R})$$

The Schrödinger equation is

$$H\Psi(\vec{r},\vec{R}) = E\Psi(\vec{r},\vec{R})$$

$$\sum_m H\Phi_m(\vec{R})\psi_m(\vec{r},\vec{R}) = E\sum_m \Phi_m(\vec{R})\psi_m(\vec{r},\vec{R})$$

$$\sum_m \underbrace{\left(\int \psi_l^*(\vec{r},\vec{R})H\psi_m(\vec{r},\vec{R})d\vec{r}\right)}_{H_{lm}}\Phi_m(\vec{R}) = E\underbrace{\left(\int \psi_l^*(\vec{r},\vec{R})\psi_m(\vec{r},\vec{R})d\vec{r}\right)}_{\delta_{lm}}\Phi_m(\vec{R})$$

Hence,

$$\sum_m H_{lm}\Phi_m(\vec{R}) = E\Phi_l(\vec{R})$$

Now,

$$H_{lm} = \int \psi_l^*(\vec{r},\vec{R})\left(-\frac{1}{2M_N}\nabla_R^2 - \frac{1}{2m_e}\nabla_r^2 + V_N(\vec{R}) + V_e(\vec{r},\vec{R})\right)\psi_m(\vec{r},\vec{R})d\vec{r}$$

$$= -\frac{1}{2M_N}\int \psi_l^*(\vec{r},\vec{R})\nabla_R^2\psi_m(\vec{r},\vec{R})d\vec{r} + \int \psi_l^*(\vec{r},\vec{R})\left(-\frac{1}{2m_e}\nabla_r^2 + V_e(\vec{r},\vec{R})\right)\psi_m(\vec{r},\vec{R})d\vec{r} +$$

$$+V_N(\vec{R})\int \psi_l^*(\vec{r},\vec{R})\psi_m(\vec{r},\vec{R})d\vec{r}$$

Using $\nabla^2(fg) = (\nabla^2 f)g + 2\nabla f\cdot\nabla g + f(\nabla^2 g)$, we obtain

$$\int \psi_l^*(\vec{r},\vec{R})\nabla_R^2\psi_m(\vec{r},\vec{R})d\vec{r} = \langle l(\vec{R})|\nabla_R^2|m(\vec{R})\rangle + 2\langle l(\vec{R})|\nabla_R|m(\vec{R})\rangle\cdot\nabla_R + \delta_{lm}\nabla_R^2$$

Also,

$$\int \psi_l^*(\vec{r},\vec{R}) \left(-\frac{1}{2m_e}\nabla_r^2 + V_e(\vec{r},\vec{R}) + V_N(\vec{R})\right) \psi_m(\vec{r},\vec{R}) d\vec{r} = \int \psi_l^*(\vec{r},\vec{R})\epsilon_m(\vec{R})\psi_m(\vec{r},\vec{R}) d\vec{r} = \epsilon_m(\vec{R})\delta_{lm}$$

Combining these results in

$$H_{lm} = -\frac{1}{2M_N}\left(\delta_{lm}\nabla_R^2 + 2\langle l(\vec{R})|\nabla_R|m(\vec{R})\rangle \cdot \nabla_R + \langle l(\vec{R})|\nabla_R^2|m(\vec{R})\rangle\right) + \delta_{lm}\epsilon_m(\vec{R})$$

(b) In the Born–Oppenheimer approximation,

$$H_{lm}(\vec{R}) \longrightarrow \delta_{lm} H_m(\vec{R})$$

Clearly,

$$H_m(\vec{R}) = -\frac{1}{2M_N}\left(\nabla_R^2 + 2\langle m(\vec{R})|\nabla_R|m(\vec{R})\rangle \cdot \nabla_R + \langle m(\vec{R})|\nabla_R^2|m(\vec{R})\rangle\right) + \epsilon_m(\vec{R})$$

Now, let

$$\vec{A}_m(\vec{R}) = i\langle m(\vec{R})|\nabla_R|m(\vec{R})\rangle$$

denote the effective vector potential. We also have a gauge freedom here which we use to set $\nabla_R \cdot \vec{A} = 0$, i.e. we chose the transverse gauge for $\vec{A}$. This can be done for the same reasons as in standard electromagnetism, that the equation $\nabla^2\phi = \nabla \cdot \vec{A}$ always has a solution.

Then, we have

$$\left(\nabla_R - i\vec{A}_m(\vec{R})\right)^2 = \nabla_R^2 - 2i\vec{A}_m\nabla_R - \vec{A}_m\vec{A}_m = \nabla_R^2 + 2\langle m(\vec{R})|\nabla_R|m(\vec{R})\rangle \cdot \nabla_R + \langle m(\vec{R})|\nabla_R^2|m(\vec{R})\rangle$$

Hence,

$$H_m(\vec{R}) = -\frac{1}{2M_N}\left(\nabla_R^2 - i\vec{A}_m(\vec{R})\right)^2 + \epsilon_m(\vec{R})V_m(\vec{R})$$

(c) We just proved that

$$V_m(\vec{R}) = \epsilon_m(\vec{R})$$

(d)

$$\vec{A}_m(\vec{R}) = i\langle m(\vec{R})|\nabla_R|m(\vec{R})\rangle$$

We have to show that it is real. First,

$$0 = \nabla_R\langle m(\vec{R})|m(\vec{R})\rangle = \langle \nabla_R m(\vec{R})|m(\vec{R})\rangle + \langle m(\vec{R})|\nabla_R|m(\vec{R})\rangle = 2\,\mathrm{Re}\langle m(\vec{R})|\nabla_R|m(\vec{R})\rangle$$

This means that $\langle m(\vec{R})|\nabla_R|m(\vec{R})\rangle$ is purely imaginary. Hence $\vec{A}_m(\vec{R})$ is real.

The Berry phase associated to a path C can be computed by

$$\gamma_m(C) = i \int_C \langle m(\vec{R}) | \nabla_R | m(\vec{R}) \rangle \cdot d\vec{R} = \int_C \vec{A}_m(\vec{R}) \cdot d\vec{R}$$

(e) First we fix $\vec{R}$ and find the eigenwavefunctions and energies of the electrons. Since the vibrational and rotational modes have much lower energies than the excitations of the electrons, we only compute the electronic groundstate (e.g. by variational techniques). Then, we compute the quantities $V_m(\vec{R})$ and $\vec{A}_m(\vec{R})$. Finally, we may find the vibrational and rotational modes by solving

$$H_m(\vec{R})\Phi_m(\vec{R}) = E_m(\vec{R})\Phi_m(\vec{R})$$