Physics 522. Quantum Mechanics II

Problem Set #3

Due Tuesday, Feb. 15, 2011

Problem 1: Periodic Potentials, Bloch Functions, and Band Structure (20 points)
Consider a periodic potential in one dimension $V(x) = V(x + L)$ (e.g. electron moving in a crystal lattice). There is a natural symmetry corresponding to translation by a lattice constant,

$$\hat{T}_L^\dagger \hat{x} \hat{T}_L = \hat{x} + L.$$

(a) Show that this symmetry satisfies,

$$\hat{T}_L^\dagger = \hat{T}_{-L}, \ \left(\hat{T}_L\right)^l = \hat{T}_{lL}.$$

(b) Show that the Hamiltonian is invariant under this symmetry, and thus these operators share a set of common eigenstates.

(c) Show that the eigenvalue equation for $\hat{T}_L$ can be written

$$\hat{T}_L \left|\psi_q\right\rangle = e^{-iqL} \left|\psi_q\right\rangle \text{ (Bloch's theorem).}$$

The eigenvector is generally written as $\left|\psi_q\right\rangle = e^{iq\hat{x}} \left|\phi_q\right\rangle$ (the Bloch state), where $\hat{T}_L \left|\phi_q\right\rangle = \left|\phi_q\right\rangle$, i.e. $\phi_q(x)$ is a periodic function of x with the lattice period (known as the Bloch function). Show that this form of $\left|\psi_q\right\rangle$ satisfies the eigenvalue above.

Thus, the eigenstates are plane wave modulated by a period function. The parameter q is known as the "quasimomemtum".

(d) We seek eigenfunctions of the Hamiltonian that are Bloch states,

$$\hat{H} \left|\psi_{n,q}\right\rangle = E_n(q) \left|\psi_q\right\rangle,$$

where n is a discrete index. The function $E_n(q)$ is known as the "energy band". Show that

$$E_n(q) = E_n(q + K),$$

where $K = 2\pi / L$ is known as the "reciprocal lattice vector". The quasi-momenta in the range

$-K/2 < q \le K/2$ is known as the "First Brillouin zone". The non-connected regions $(K/2, K] + (-K, -K/2]$ form the second Brillouin zone, etc.

(e) Let us write the potential as sum of wells localized at each lattice site, $V(x) = \sum_l v(x + lL)$. The single well has a discrete set of bound states,

$$\left(\frac{p^2}{2m} + v(x) \right) u_n(x) = E_n^{(0)} u_n(x).$$

Consider a situation in which the electrons are tightly bound at the given lattice sites (i.e. deep in the valance band). The electron can travel to a neighboring site only by tunneling through a barrier. Assuming weak tunneling, a zeroth approximation to the energy band is to place "single atom orbital", $u_n(x)$ at each lattice site, consistent with Bloch's theorem. (Next page)

Show that $\left|\psi_{n,q}^{(0)}\right\rangle = \sum_{l=-\infty}^{\infty} e^{ilqL} \hat{T}_{lL} \left|u_n\right\rangle$ satisfy Bloch's theorem. To first order in perturbation theory in the "tight-binding" approximation show that,

$$E_n(q) = E_n^{(0)} + 2\Delta E_n \cos(qL)$$

where $\left\langle u_n \middle| \hat{H} \hat{T}_L \middle| u_n \right\rangle \equiv \Delta E_n$ (taken to be real).

(f) Consider the specific example of a sinusoidal potential, $V(x) = V_0(1 - \cos(2kx))/2$, as in an optical lattice. In the tight-binding approximation, under the assumption the single particle orbitals are well approximated by a harmonic approximation to the potential, sketch the real and imaginary parts of the wave function for $q = 0, K/4, K/2$ (i.e. center and edge of the first Brillouin zone and half-way to the edge). Sketch the ground and first excited energy bands $E_n(q)$ in the first Brillouin zone.

Now let us go the opposite limit in which the potential is very weak, i.e. near to a free electron gas, so the wave functions are close to plane waves. This is valid for the conduction bands in a solid. Start by expressing the *exact* TISE in the plane wave basis. Because the potential is periodic, i.e. can be expanded as a discrete Fourier series, $V(x) = \sum_l v_l e^{il(Kx)}$, and the same for the Bloch function $\phi_{nq}(x) = \sum_l c_l^{(nq)} e^{il(Kx)}$.

(g) Show that the expansion coefficients satisfy,

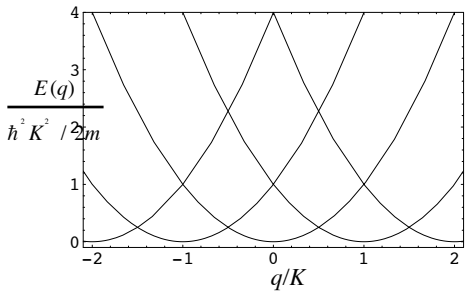
$$c_l^{(nq)} \left(\frac{\hbar^2 (q + lK)^2}{2m} - E_n(q) \right) + \sum_{l'} c_{l-l'}^{(nq)} v_{l'} = 0.$$

(h) Consider the *free* electron problem in 1D (i.e. $V(x)=0$). This is also a periodic potential (trivial of course). Argue for each l we must have,

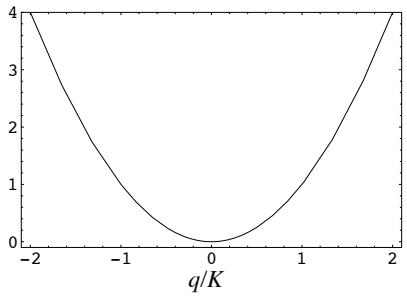
$E_n(q) = \frac{\hbar^2 (q + lK)^2}{2m}$. Does this agree with your expectation of free particle? Explain.

Of course here $K = \frac{2\pi}{L}$ is arbitrary, since there is no real period L.

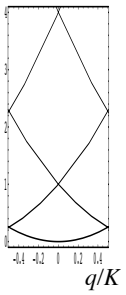
A plot of the energy "bands" is typically done in three different way shown below.



"repeated zone"



"extended zone"



"reduced zone"

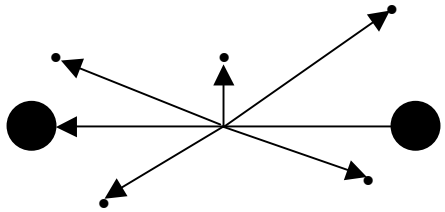
Note that the energy bands are degenerate at the center and edge of each Brillouin zone ($q/K=n/2$). In the repeated zone scheme we explicitly see the periodicity of the bands (here over 4 zones). In the extended zone scheme we plot each band in its corresponding Brillouin zone (first band--> first Brillouin zone), (second band --> second Brillouin zone), etc. In the reduced zone scheme, we plot all bands only in the first Brillouin zone, which contains all information.

(i) Now treat the periodic potential as a *perturbation* to the free particle solution above. Show that gaps open at the degenerate points (i.e. crossings become anti-crossings) with an energy gap of $2v_1$. Sketch the band structure in the three schemes as in (h).

Problem 2: The Born-Oppenheimer Approximation and Landau-Zener (10 Points)

We have discussed in class adiabatic change of a Hamiltonian due an *externally controlled classical parameter*. Another important scenario is when we have coupled degrees of freedom which are *quantum* but have different dynamical time scales. If one scale is much faster than the other, the dynamics of the fast variable is "slaved" to the slow variable. That is, it the quick system adiabatically follows the slow one.

The standard paradigm for this circumstance in quantum mechanics is the dynamics of molecules. For example, consider a diatomic molecule, i.e. two nuclei with constituent electrons.



The Hamiltonian for the system (in the center of mass frame) is

$$\hat{H} = \hat{T}_R + \hat{T}_e + \hat{V}_e(\{\mathbf{r}_i\}) + \hat{V}_N(R) + \hat{V}_{e,N}(\{\mathbf{r}_i\},R),$$

where $\hat{T}_R$ and $\hat{T}_e$ are the kinetic energies of the relative coordinate of the nuclei and the electrons, respectively, $\hat{V}_N(R)$ and $\hat{V}_e(\{\mathbf{r}_i\})$ are the coulomb repulsion potentials between the nuclei and between the electrons, and $\hat{V}_{e,N}(\{\mathbf{r}_i\},R)$ is the coulomb attraction between the nuclei and electrons. This is a complex many body problem that is generally impossible to solve. However, the nuclei are much much heavier than the electrons, and therefore move much slower than the speedy light electrons. Thus, the electrons will *adiabatically* follow the nuclei. We can take this into account quantum mechanically as follows.

- Diagonalizable $\hat{H}$ *ignoring* the nuclear motion. Thus, we treat the internuclear coordinate *R* as a classical parameter

$$\left(\hat{T}_e + \hat{V}_e(\{\mathbf{r}_i\}) + \hat{V}_N(R) + \hat{V}_{e,N}(\{\mathbf{r}_i\},R)\right)\phi_n(\{\mathbf{r}_i\},R) = U_n(R)\ \phi_n(\{\mathbf{r}_i\},R).$$

The eigenvalues $U_n(R)$, parameterized by R, are known as the adiabatic potentials. Since this is a complete set for the electron space at any R, an exact expansion of the total wave function for electrons and nuclei is

$$\Psi(\{\mathbf{r}_i\},R) = \sum_n \eta_n(R)\phi_n(\{\mathbf{r}_i\},R).$$

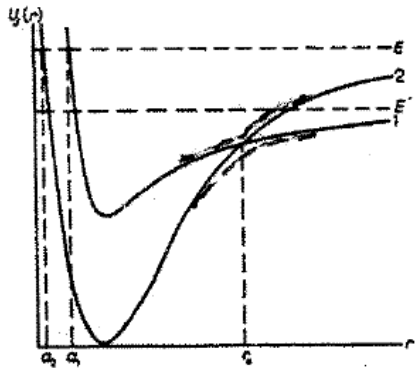
This is known as the solution to the TISE in the adiabatic basis.

(a) Argue that in an adiabatic approximation

$$\hat{T}_R \sum_n \eta_n(R)\phi_n(\{\mathbf{r}_i\},R) \approx \sum_n \left(\hat{T}_R \eta_n(R)\right)\phi_n(\{\mathbf{r}_i\},R)$$

so that the TISE reduces to $\left(\hat{T}_R + U_n(R)\right)\eta_n(R) = E\eta_n(R)$ for *each* adiabatic state. This is known as the *Born-Oppenheimer* approximation (the adiabatic potentials are sometime known as the Born-Oppenhemier potentials). Note that under the BO approximation, the wave function for electrons and nuclei separates as $\Psi(\{\mathbf{r}_i\},R) = \eta_n(R)\phi_n(\{\mathbf{r}_i\},R)$.

The nuclei generally move adiabatically in the BO potentials for a given electron configuration. But suppose as some critical radius two BO potentials cross, as shown below. If the they are coupled, this crossing can become an avoided crossing.



Near the crossing, the neglected terms in the BO approximation can now become important determine whether or not the nuclei move adiabatically or diabatically through the crossing. For example, nuclei moving in BO potential 1 might adiabatically transfer to state 2 and dissociate, below the usual energy threshold. This phenomenon is known as "predissociation"

(b) Argue that if the relative velocity of the nuclei through the crossing region is v, the probability for a diabatic transition is

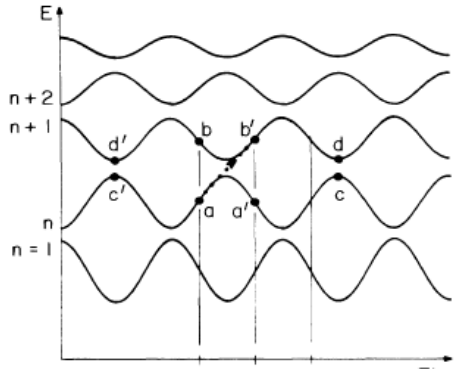
$P_{diab} = e^{-2\pi A}$, where $A = \dfrac{V_{12}^2}{\hbar v \left| F_1 - F_2 \right|}$ with V_{12} the coupling matrix element and

$F_i = -\dfrac{dU_i(R_c)}{dR}$ is the force on the nuclei in the i^{th} BO potential.

(Hint: Approximate the anti-crossing as the standard hyperbola discussed in class for the spin 1/2 in a magnetic field).

(c) **5 points Extra Credit**

Another example is the so called "Zener breakdown" of the conduction of electrons in crystalline solids. The energy bands provide a dispersion relation $\omega_n(q) = E_n(q)/\hbar$ so that electrons in the n band and quasimomentum q move with a group velocity $v = d\omega_n(q)/dq$. Now if we apply an electric field $\mathcal{E}$, the electron will accelerate. Assuming the acceleration is sufficiently slow, the electron will adiabatically follow in its energy band $q(t) = q(0) - e\mathcal{E}t/\hbar$. However, at the edge of the Brillouin zone, there is an anticrossing. If the electron is moving too fast it will "tunnel" (i.e. make a diabatic LZ transition) to the next band



Thus, a insulator with a large bandgap will start to conduct. This is "Zener break down". Show that the rate of tunneling (and thus the current per charge) is

$$\gamma = \frac{e\mathcal{E}L}{2\pi\hbar}\exp\left\{-\frac{m_e L\,\delta^2}{\hbar^2 e\mathcal{E}}\right\}$$

where L is that lattice period and δ is the half width of the energy gap.