Nearly Free Electron Model

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1 Summary of Time Independent Perturbation Theory of QM

[It is very important to be reminded of this firmly, before dealing with the nearly free electron theory.]

Say that we have Hamiltonian H_0 which we assume is completely diagonalized by basis $|n_0\rangle$ with energy eigenvalue ε_{n0}, that is, we have

$$H_0|n_0\rangle = \varepsilon_{n0}|n_0\rangle$$

Let us say that the total Hamiltonian H is given as

$$H = H_0 + H_1 \text{ where } H_1 \ll H_0$$

(The meaning of $H_1 \ll H_0$ will be given below.) Perturbation theory assumes that the exact eigenstate of H can be obtained from $|n_0\rangle$ by adding small modifications, which are due to H_0.

1.1 Non-Degenerate Case

What is really meant by $H_1 \ll H_0$ in perturbation theory is that the matrix elements of H_1 are small compared to level spacings concerned. The non-degenerate case is when this condition simply holds to start with. The energy eigenvalue of the n^{th} level $|n\rangle \approx |n_0\rangle$ is given by

$$\varepsilon_n \approx \varepsilon_{n0} + \langle n_0|H_1|n_0\rangle + \sum_{m\neq n} \frac{|\langle n_0|H_1|m_0\rangle|^2}{\varepsilon_{n0} - \varepsilon_{m0}}$$

1.2 Degenerate Case

Let us say that there are two states $|n_0\rangle, |n_0'\rangle$, which are degenerate. [Generalization to the case of higher degeneracy is straightforward.] You can see thaat this is problematic, since, in contrast to the non-degenerate case, we cannot say that energy level spacings (which is 0 between $|n_0\rangle, |n_0'\rangle$) are smaller than matrix elements of H_1. Here is how this problem can handled. First, solve 2×2 matrix for the submatrix of H using the basis set of $|n_0\rangle, |n_0'\rangle$. Let us call the eigenstates of this submatrix $|n_D\rangle, |n_D'\rangle$ with respective eigenvalues $\varepsilon_{n0} + \varepsilon^{(1)}_{nD}$ and $\varepsilon_{n0} + \varepsilon^{(1)}_{n'D}$. Second, the eigenvalue of $|n\rangle \approx |n_D\rangle$ up to 2nd order is then given by

$$\varepsilon_n \approx \varepsilon_{n0} + \varepsilon^{(1)}_{nD} + \sum_{m\neq n,n'} \frac{|\langle n_D|H_1|m_0\rangle|^2}{\varepsilon_{nD} - \varepsilon_{m0}}$$

The eigenvalue for $|n'\rangle \approx |n_D'\rangle$ is similarly given by $\varepsilon_{n'} \approx \varepsilon_{n0} + \varepsilon^{(1)}_{n'D} + + \sum_{m\neq n,n'} \frac{|\langle n_D'|H_1|m_0\rangle|^2}{\varepsilon_{n'D} - \varepsilon_{m0}}$. This result is sometimes stated as "eigenvalues of the submatrix give the first order approximation." Also, note that in the sum for the 2nd order correction, the indices for the submatrix basis set are excluded, that is both n, n' not just n or n'. [This scheme can fail, if the submatrix of H, after diagonalization, does not break the degeneracy of n, n' since $|n_D\rangle$ and $|n_D'\rangle$ are still ambiguous then.]

2 Nearly Free Electron Model

Let us now consider the case of nearly free electrons in crystal. H_0 is the kinetic energy term and H_1 is the crystal potential term. Unperturbed states are $|\vec{k}\rangle$ where $\hbar\vec{k}$ is momentum (crystal momentum when we are done with the problem). It is important to note that

$$\langle\vec{k}'|H_1|\vec{k}\rangle \neq 0 \,\text{only if}\, \vec{k}' = \vec{k} + \vec{G} \,\text{where}\, \vec{G} \,\text{is some R.L. vector} \tag{1}$$

[This is basically a statement about the Fourier transform, and is more generally applicable even when H_1 is not small, laying the physical basis for the Bloch theorem.] I will often use the notation

$$V_{\vec{G}} \equiv \langle\vec{k} + \vec{G}|H_1|\vec{k}\rangle \tag{2}$$

Non-degenerate case For $|\vec{k}\rangle$ that is not degenerate with other free electron states coupled by $\vec{G}$, the energy value, within the 2nd order perturbation theory, is simply

$$\varepsilon_{\vec{k}} = \varepsilon^0_{\vec{k}} + V_0 + \sum_{\vec{G}\neq 0} \frac{|V_{\vec{G}}|^2}{\varepsilon^0_{\vec{k}} - \varepsilon^0_{\vec{k}+\vec{G}}} \tag{3}$$

where $\varepsilon^0_{\vec{k}}$ is the free electron energy $\frac{\hbar^2\vec{k}^2}{2m}$.

Degnerate case Consider $|\vec{k}\rangle$ and $|\vec{k} + \vec{G}\rangle$ that are degnerate (with $\vec{G} \neq 0$, of course), as would be the case for $\vec{k}$ on BZ boundaries. [We spare ourselves of the more complicated case when triple or quadruple etc degenercy exists. They just require diagonalization of higher dimensional maxtrices.] The submatrix of H is then written as

$$\begin{bmatrix} \varepsilon^0_{\vec{k}} + V_0 & V^*_{\vec{G}} \\ V_{\vec{G}} & \varepsilon^0_{\vec{k}} + V_0 \end{bmatrix} \tag{4}$$

The eigenvalue of this submatrix gives the 1st order correction in energy. The 2nd order correction is given as explained above. Collecting the two we have

$$\varepsilon_{\vec{k}} = \varepsilon^0_{\vec{k}} + V_0 \pm |V_{\vec{G}}| + \sum_{\vec{G}'\neq 0,\vec{G}} \frac{|V_{\vec{G}'}|^2}{\varepsilon^0_{\vec{k}} - \varepsilon^0_{\vec{k}+\vec{G}'}} \tag{5}$$

For weak potential, the 2nd order term can be ignored and we get

$$\varepsilon_{\vec{k}} = \varepsilon^0_{\vec{k}} + V_0 \text{ (non-degenerate)}, \; \varepsilon^0_{\vec{k}} + V_0 \pm |V_{\vec{G}}| \text{ (degenerate)} \tag{6}$$

Note that in equations 3,5,6 V_0 is a $\vec{k}$-independent shift in energy, which can be ignored for many purposes. Thus, one sees that within the first order, the only thing that happens is the splitting into bonding and antibonding levels in the case of the degenerate case. [Question: If $\varepsilon^0_{\vec{k}} \neq \varepsilon^0_{\vec{k}+\vec{G}}$, but $|\varepsilon^0_{\vec{k}} - \varepsilon^0_{\vec{k}+\vec{G}}| \ll |V_{\vec{G}}|$, then which approach (ND or D) should you be using? – Answer is in the "abolute essential" note.]