561 F 2005 Lecture 2
Background and notation

Basic Equations for Interacting Electrons and Nuclei

The goal of this course is to describe properties of condensed matter using concepts and theoretical methods firmly rooted in the fundamental equations. Thus our starting point is the hamiltonian for the system of electrons and nuclei,

$$\begin{aligned}\hat{H} = & - \sum_i \frac{\hbar^2}{2m_e}\boldsymbol{\nabla}_i^2 - \sum_{i,I} \frac{Z_I e^2}{|\mathbf{r}_i - \mathbf{R}_I|} + \frac{1}{2}\sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} \\ & - \sum_I \frac{\hbar^2}{2M_I}\boldsymbol{\nabla}_I^2 + \frac{1}{2}\sum_{I \neq J} \frac{Z_I Z_J e^2}{|\mathbf{R}_I - \mathbf{R}_J|},\end{aligned} \tag{1}$$

where lower case letters denote the electrons and capital letters, the nuclei of charge Z_I and mass M_I. (Here we ignore relativistic effects and magnetic fields.) The hamiltonian can be written

$$\hat{H} = \hat{T}_N + \hat{T}_e + \hat{U} \equiv \hat{T}_N + \hat{H}_e, \tag{2}$$

where the electron hamiltonian $\hat{H}_e$ contains all the potential terms $\hat{U}$. (The nucleus-nucleus interaction is included for convenience; it is just an added energy E_{II} independent of electron coordinates.) We will use atomic units where $\hbar = m_e = e = 1$, so the the equations simplify and the nuclear kinetic energy becomes $\hat{T}_N = \sum_I \frac{m_e}{2M_I}\boldsymbol{\nabla}_I^2$.

Adiabatic or Born-Oppenheimer Approximation

See Martin, Appendix C on "Adiabatic Approximation"; Phillips, Ch. 2; Pines, Ch. 5; Ziman, Prin. Th. Of Solids, p. 169-172; Born and Huang, Appendix VIII.

There is only one small parameter in the problem, the mass ratio $\frac{m_e}{M_I}$. Therefore we start with analysis which uses only this fact and no other approximations. If we first set the mass of the nuclei to infinity, then the kinetic energy of the nuclei can be ignored. This is the Born–Oppenheimer or adiabatic approximation, which is an excellent approximation for many purposes, e.g., the calculation of nuclear vibration modes in most solids. This leads to division of "low energy scales for nuclear motion" in which the electronic states "follow the nuclei" adiabatically remaining in their instantaneous ground states, and "high energy scales for electrons" that describe the electronic excitations.

As discussed by Phillips, Ch 2, the nuclei tend to be much more localized around sites than the electrons. This is easy to understand since the energy as a function of position is similar for electrons and nuclei, but the nuclear mass is much larger leading to smaller displacements δ. Simple arguments suggest $\delta \propto a(m_e/M_I)^{1/4}$, where a is the distance between atoms. This is roughly $(10^{-4})^{1/4} \propto 1/10$, much larger than stated by Phillips, but still small.

Elementary Excitations Condensed Matter 1: Electronic states at fixed positions on the nuclei

Thus we focus on the hamiltonian for the electrons, in which the positions of the nuclei are parameters. This specifies the electronic problem which leads to the electronic states at fixed nuclear positions $\{\mathbf{R}\}$:

$$\hat{H}_e(\{\mathbf{R}\})\Psi_i(\{\mathbf{r}\}:\{\mathbf{R}\}) = E_i(\{\mathbf{R}\})\Psi_i(\{\mathbf{r}\}:\{\mathbf{R}\}). \tag{3}$$

This is the many-body equation for interacting electrons in the presence of fixed nuclei or other fixed external potentials - the key fundamental problem for this course.

Elementary Excitations Condensed Matter 2: Nuclear Vibrations

The full solutions for the coupled system of nuclei and electrons

$$\hat{H}\Psi_s(\{\mathbf{r},\mathbf{R}\}) = E_s\Psi_s(\{\mathbf{r},\mathbf{R}\}), \tag{4}$$

where $s = 1, 2, 3, \ldots,$ labels the states of the coupled system, can be written in terms of $\Psi_i(\{\mathbf{r}\}:\{\mathbf{R}\})$,

$$\Psi_s(\{\mathbf{r},\mathbf{R}\}) = \sum_i \chi_{si}(\{\mathbf{R}\})\Psi_i(\{\mathbf{r}\}:\{\mathbf{R}\}), \tag{5}$$

since $\Psi_i(\{\mathbf{r}\}:\{\mathbf{R}\})$ defines a complete set of states for the electrons at each $\{\mathbf{R}\}$.

The states of the coupled electron–nuclear system are now specified by $\chi_{si}(\{\mathbf{R}\})$, which are functions of the nuclear coordinates and are the coefficients of the electronic states $\Psi_m i$. In order to find the equations for $\chi_{si}(\{\mathbf{R}\})$, insert expansion (5) into (4), multiply the expression on the left by $\Psi_i(\{\mathbf{r},\mathbf{R}\})$, and integrate over electron variables $\{\mathbf{r}\}$ to find the equation

$$\left[\hat{T}_N + E_i(\{\mathbf{R}\}) - E_s\right]\chi_{si}(\{\mathbf{R}\}) = -\sum_{i'} C_{ii'}\chi_{si'}(\{\mathbf{R}\}), \tag{6}$$

where the matrix elements are given by $C_{ii'} = A_{ii'} + B_{ii'}$, with

$$A_{ii'}(\{\mathbf{R}\}) = \sum_J \frac{m_e}{M_J}\langle\Psi_i(\{\mathbf{r}\}:\{\mathbf{R}\})|\boldsymbol{\nabla}_J|\Psi_{i'}(\{\mathbf{r}\}:\{\mathbf{R}\})\rangle\boldsymbol{\nabla}_J, \tag{7}$$

$$B_{ii'}(\{\mathbf{R}\}) = \sum_J \frac{m_e}{2M_J}\langle\Psi_i(\{\mathbf{r}\}:\{\mathbf{R}\})|\nabla_J^2|\Psi_{i'}(\{\mathbf{r}\}:\{\mathbf{R}\})\rangle. \tag{8}$$

Here $\langle\Psi_i(\{\mathbf{r}\}:\{\mathbf{R}\})|\mathcal{O}|\Psi_{i'}(\{\mathbf{r}\}:\{\mathbf{R}\})\rangle$ means integrations over only the electronic variables $\{\mathbf{r}\}$ for any operator $\mathcal{O}$.

The adiabatic or Born-Oppenheimer approximation is to ignore the off-diagonal $C_{ii'}$ terms, e.g., the electrons are assumed to remain in a given state m as the nuclei move. Although the electron wavefunction $\Psi_i(\{\mathbf{r}\}:\{\mathbf{R}\})$ and the energy of state m change, the electrons do not change state and no energy is transferred between the degrees of freedom described by the equation for the nuclear variables $\{\mathbf{R}\}$ and *excitations* of the electrons, which occurs only if there is a change of state $i \rightarrow i'$. The diagonal terms can be treated easily. First, it is simple to show (exercise for the reader) that $A_{ii} = 0$ simply from the requirement that Ψ is normalized. The term $B_{ii}(\{\mathbf{R}\})$ can be grouped with $E_i(\{\mathbf{R}\})$ to determine a modified potential function for the nuclei $U_i(\{\mathbf{R}\}) = E_i(\{\mathbf{R}\}) + B_{ii}(\{\mathbf{R}\})$.

Thus, in the adiabatic approximation, the nuclear motion is described by a purely nuclear equation for each electronic state i

$$\left[-\sum_J \frac{m_e}{2M_J} \nabla_J^2 + U_i(\{\mathbf{R}\}) - E_{ni} \right] \chi_{ni}(\{\mathbf{R}\}) = 0, \tag{9}$$

where $n = 1, 2, 3, \ldots,$ labels the nuclear states. Within the adiabatic approximation, the full set of states $s = 0, i, \ldots,$ is a product of nuclear and electronic states.

So long as we can justify neglecting the off-diagonal terms that couple different electron states, we can solve the nuclear motion problem, Eq. (9), given the function $U_i(\{\mathbf{R}\})$ for the particular electronic state i that evolves adiabatically with nuclear motion. This is an excellent approximation except for cases where there is degeneracy or near degeneracy of the electronic states. If there is a gap in the electronic excitation spectrum much larger than typical energies for nuclear motion, then the nuclear excitations are well determined by the adiabatic terms. Special care must be taken for cases such as transition states in molecules where electronic states become degenerate, or in metals where the lack of an energy gap leads to qualitative effects.

The solution of this problem is to expand in terms of displacements, leading to harmonic and anharmonic oscillator hamiltonians. (See, for example, Born and Huang, Pines Ch. 2, and Doniach Ch 1.) Define displacements of the atoms from their equilibrium positions, $R_I = R_I^0 + u_I$, and expand the potential energy in powers of u_I,

$$E_0(\{R_I\}) = E_0(\{R_I^0\}) + \frac{1}{2} \sum D_{IJ}^{\alpha\beta} u_I^{\alpha} u_J^{\beta} + \ldots \tag{10}$$

where the linear terms vanish, the D's are second derivatives, etc. The exact eigenstates can be written as $\chi_m(\{u_I\})$.

Elementary Excitations Condensed Matter 3: Electron-Phonon coupling

Electron-phonon interactions result from the off-diagonal matrix elements $C_{ii'}$ that describe transitions between different electronic states due to the velocities of the nuclei. The dominant terms are given in Eq. (7), which involves a gradient of the electron wavefunctions with respect to the nuclear positions and the gradient operator acting on the phonon wavefunction χ. Combination of these operators leads to an electronic transition between states i and i' coupled with emission or absorption of one phonon.

The terms are indeed generally small with the largest $\propto \delta^2 \propto (m_e/M_I)^{-1/2}$

The steps involved in writing the expressions for the matrix elements are: 1) to express the nuclear kinetic operator $\boldsymbol{\nabla}_J$ in Eq. (7) in terms of phonon creation and annihilation operators, and 2) to write out the perturbation expression for the matrix element. The latter step can be accomplished by noting that the variation in the electron function due to the displacement of nucleus J is caused by the change in potential due to the displacement. To linear order the relation is

$$\langle \Psi_i(\{\mathbf{r}\} : \{\mathbf{R}\}) | \boldsymbol{\nabla}_J | \Psi_{i'}(\{\mathbf{r}\} : \{\mathbf{R}\}) \rangle = \frac{\langle \Psi_i(\{\mathbf{r}\}:\{\mathbf{R}\}) | \boldsymbol{\nabla}_J V | \Psi_{i'}(\{\mathbf{r}\}:\{\mathbf{R}\}) \rangle}{E_{i'}(\{\mathbf{R}\}) - E_i(\{\mathbf{R}\})}. \tag{11}$$

This leads to the form of the electron-phonon matrix elements (treated in second quantization later) that are the basis for understanding electrical transport in metals, polaron formation in insulators, and the BCS theory of superconductivity.

Force (Hellmann-Feynman) Theorem

(Ref. R. P. Feynman, Phys Rev 56, 530 (1939), and many texts. The first derivation is probably P. Eherenfest, Z. Phys. 1927, where he proved this theorem as part of the correspondence principle of quantum and classical mechanics.)

Derivatives of the energy with respect to a parameter λ can always be written

$$\frac{\partial E}{\partial \lambda} = \langle \Psi_0 | \frac{\partial H}{\partial \lambda} | \Psi_0 \rangle \tag{12}$$

using the fact that the energy is stationary in the ground state wavefunction Ψ_0. Thus within the adiabatic approximation, the force on any atom is given simply by

$$\mathbf{F}_I = -\frac{\partial E}{\partial \mathbf{R}_I} = -\int d^3r \rho(\mathbf{r}) \frac{\partial V_{Ion-elec}(\mathbf{r})}{\partial \mathbf{R}_I} - \frac{\partial E_{Ion-Ion}}{\partial \mathbf{R}_I}. \tag{13}$$

This gives the force strictly in terms of Coulomb interactions with the average electron (and ion) density independent of electron-electron correlations and interactions.

Similarly, there are expressions for the pressure from the virial theorem in terms of the ground state.

The same reasoning as that for the Force Theorem leads to the well-known coupling constant integration formulas. Let us define a parameter in the hamiltonian λ such that $\lambda = 0$ corresponds to a simple hamiltonian such as non-interacting particles and $\lambda = 1$ corresponds to the full complicated hamiltonian such as interacting particles. By integrating from $\lambda = 0$ to $\lambda = 1$ one can find the change in energy from the integral of the force times $d\lambda$,

$$\Delta E = \int_{\lambda_1}^{\lambda_2} \mathrm{d}\lambda \frac{\partial E}{\partial \lambda} = \int_{\lambda_1}^{\lambda_2} \mathrm{d}\lambda \langle \Psi_\lambda | \frac{\partial \hat{H}}{\partial \lambda} | \Psi_\lambda \rangle. \tag{14}$$

For example, if a parameter such as the charge squared of the electron e^2 in the interaction energy in the hamiltonian is scaled by $e^2 \rightarrow e^2\lambda$, then λ can be varied from 0 to 1 to vary the hamiltonian from the non-interacting limit to the fully interacting problem.

Summary

Division of excitations of condensed matter into:

- Low energy "screened" motion of the nuclei
- Many-body correlated motion of nuclei which describe vibrations and structural phase transitions
- Higher energy excitations of the electrons - EXCEPT for the low energy excitations near the Fermi energy of a metal
- Adiabatic Approximation in which electrons follow the nuclei adiabatically
- The Force Theorem (Hellmann-Feynman Theorem)
- The effects of the terms omitted in the adiabatic approximation: the scattering of electrons between different electronic states due to lattice vibrations - important for transport; the resulting many-body problem leads to superconductivity
- Other interesting cases where electrons develop low energy scales, in strongly-correlated systems