Condensed Matter Physics

PHY 5111

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Electron-Electron Interactions

Condensed Matter Physics – Michael P. Marder

Chapter 9

What did we learn so far?

$$\hat{\mathcal{H}} = \sum_l \frac{\hat{P}_l^2}{2M_l} + \frac{1}{2} \sum_{l \neq l'} \frac{q_l q_{l'}}{|\hat{R}_l - \hat{R}_{l'}|}$$

- The Free Fermi Gas

- Single Electron Model

- Bloch's Theorem

- Kronig-Penney Model

- Nearly Free Electron Model

- Tightly Bound Electron Model

What did we miss?

The electron-electron interactions!

If we understand **electrons**, then we understand **everything**.

(almost)

The electron-electron interactions

> ➢ Born-Oppenheimer approximation

> ➢ Hartree equation

> ➢ Hartree-Fock Equations

> ➢ Density Functional Theory

>> ▪ Hohenberg-Kohn Theorem

>> ▪ Hohenberg and Kohn

>> ▪ Kohn-Sham Equations

Born-Oppenheimer approximation (1927)

Because nuclei are thousands of times more massive than electrons, they move that much more slowly.

$$\hat{\mathcal{H}}\Psi = \frac{-\hbar^2}{2m}\sum_{l=1}^{N}\nabla_l^2\Psi + \sum_{l=1}^{N}U_{\text{ion}}(\vec{r}_l)\Psi + \sum_{l<l'}\frac{e^2}{|\vec{r}_l - \vec{r}_{l'}|}\Psi = \mathcal{E}\Psi,$$

Born-Oppenheimer approximation

So far as the electrons are concerned, take the nuclei to be static, classical potentials, and solve the electronic problem without worrying about the nuclei further. So far as the nuclei are concerned, the electrons are a rapidly moving shroud of charge that follows them wherever they go. Because the motion of nuclei is accompanied by charge redistribution, the energies involved in moving nuclei about depend upon the solution of the electron problem, and the nuclei interact with complicated effective potentials.

Hartree equation

All the computational difficulty arises from the Coulomb interaction. Perhaps this term may somehow be replaced by something more computationally tractable, such as an effective electron–electron potential $U_{ee}(\vec{r})$. A first guess at such an effective potential in which to study the motion of electrons is that each electron moves in a field produced by a sum over all the other electrons. Analogy with classical physics suggests that the potential corresponding to electron–electron interactions could be

$$U_{ee}(\vec{r}) = \int d\vec{r}' \frac{e^2 n(\vec{r}')}{|\vec{r} - \vec{r}'|},$$

where n is the number density of electrons

$$n(\vec{r}) = \sum_j |\psi_j(\vec{r})|^2.$$

Hartree equation

$$\frac{-\hbar^2}{2m}\nabla^2\psi_l + [U_{\text{ion}}(\vec{r}) + U_{\text{ee}}(\vec{r})]\psi_l = \varepsilon_l\psi_l.$$

$$U_{\text{ee}}(\vec{r}) = \int d\vec{r}' \frac{e^2 n(\vec{r}')}{|\vec{r}-\vec{r}'|}, \qquad n(\vec{r}) = \sum_j |\psi_j(\vec{r})|^2.$$

Hartree equation

The central failing of the Hartree equation is that it does not recognize the **Pauli exclusion principle**. The true many-body wave function must vanish whenever two electrons occupy the same position, but the Hartree wave function cannot have this property. The Pauli principle forces electrons in metals to occupy single-particle energy states with energies on the order of 10 000 K, even in the ground state – such large energies that this effect must be included in any calculation from the outset to have any hope of realism.

Hartree-Fock Equations

$$\Psi(\vec{r}_1\sigma_1 \ldots \vec{r}_N\sigma_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\vec{r}_1\sigma_1) & \psi_1(\vec{r}_2\sigma_2) & \ldots & \psi_1(\vec{r}_N\sigma_N) \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \cdot & \cdot & & \cdot \\ \psi_N(\vec{r}_1\sigma_1) & \psi_N(\vec{r}_2\sigma_2) & \ldots & \psi_N(\vec{r}_N\sigma_N) \end{vmatrix}$$

This type of wave function is called a *Slater determinant.*

What can be done with Hartree-Fock Equations?

One first of all has an approximation to the ground-state wave function that can be used to calculate such experimentally measurable quantities as the dipole moment.

Second of all, one has all of the excited states that were found while diagonalizing the Hartree-Fock Hamiltonian, but not included in the ground state. The lowest lying excited state provides an estimate of the ionization potential of an atom or molecule.

Third, one can calculate how the total energy of a molecule varies with the external potential and in this way try to calculate the equilibrium geometry of a molecule.

What sorts of results may be obtained by carrying out Hartree-Fock calculations?

Molecule	CH_4	NH_3	H_2O	FH	CO
Bond length (Å): Hartree–Fock	2.048	1.890	1.776	1.696	
Bond length (Å): experiment	2.050	1.912	1.809	1.733	
Ionization potential (eV): Hartree–Fock	0.546	0.428	0.507	0.650	
Ionization potential (eV): experiment	0.529	0.400	0.463	0.581	
Dipole moment (e Å): Hartree–Fock		0.653	0.785	0.764	−0.110
Dipole moment (e Å): experiment		0.579	0.728	0.716	0.044

Bond lengths, ionization potentials, and dipole moments, comparing Hartree–Fock, and experiment. In the delicate case of CO, even the sign of the dipole moment is incorrect. Source: Szabo and Ostlund (1982).

Limitations of Hartree-Fock equation

Hartree-Fock does not do particularly well at computing dipole moments. It is able to calculate only to within about 0.1 in atomic units and may even get the sign wrong, as in the case of CO. Bond lengths come out better than dipole moments, but ionization potentials are again obtained only at about a 10% level. In the case of N2, Hartree-Fock incorrectly identifies the first excited state. The molecules in this table have 10 electrons, and therefore they are rather simple test cases. Ones conclusion must be that Hartree-Fock provides only a qualitative guide and is not adequate for precise molecular calculations.

Density Functional Theory

The starting point of the theory is the observation of Hohenberg and Kohn (1964) that electron density contains in principle all the information contained in a many-electron wave function. The electronic density of a many-electron system at point $\vec{r}$ is defined to be

$$n(\vec{r}) = \langle \Psi | \sum_{l=1}^{N} \delta(\vec{r} - \vec{R}_l) | \Psi \rangle$$

$$= N \int d\vec{r}_1 \ldots d\vec{r}_N \Psi^*(\vec{r}_1, \vec{r}_2 \ldots \vec{r}_N) \delta(\vec{r} - \vec{r}_1) \Psi(\vec{r}_1 \ldots \vec{r}_N).$$

Density Functional Theory

Hohenberg and Kohn pointed out that if one knows the density of the ground state of a many-electron system, one can deduce from it the external potential in which the electrons reside, up to an overall constant. It must be kept in mind that the only ways in which two many-electron problems can differ are in the external potentials U and in the number of electrons that reside in the potentials. According to this result, both of these external parameters are determined by the electron density, so one can say that the density completely determines the many-body problem. This statement is surprising, because the density is a real function of a single spatial variable, while the complete quantum mechanical wave function needs N variables for its description.
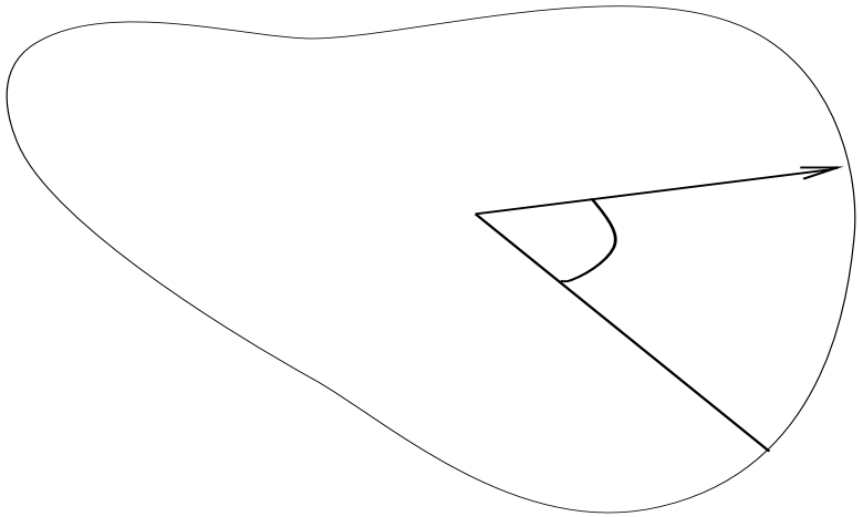
What is a functional?

A function maps one number to another.

A functional assigns a number to a function.

$$r(\theta) = 1/\sqrt{\sin^2(\theta) + 4\cos^2(\theta)}$$

$$P[r] = \int_0^{2\pi} d\theta \ \sqrt{r^2(\theta) + (dr/d\theta)^2}$$

Kohn-Sham equations

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\phi_i(\mathbf{r})|^2.$$

$$\left\{ -\frac{1}{2}\nabla^2 + v_{\mathrm{s}}(\mathbf{r}) \right\} \phi_i(\mathbf{r}) = \epsilon_i \phi_i(\mathbf{r}),$$

$$v_{\mathrm{s}}(\mathbf{r}) = v_{\mathrm{ext}}(\mathbf{r}) + \int d^3r \frac{n(\mathbf{r})}{|\mathbf{r} - \mathbf{r}'|} + v_{\mathrm{xc}}[n](\mathbf{r})$$