

G25.2651: Statistical Mechanics

Notes for Lecture 10

I. THE LOCAL DENSITY APPROXIMATION

In modern density functional theory, the total energy E of a system of electrons subject to an external potential (usually taken to be the interaction between the electrons and positively charged nuclei in a molecule), is expressed as a functional of the electron density $\rho(\mathbf{r})$. This functional is given by

$$E[\rho] = T[\rho] + W[\rho] + V[\rho]$$

where $T[\rho]$ is the kinetic energy, $W[\rho]$ is the electron-electron repulsion, and $V[\rho]$ is the external potential. Expressions for $T[\rho]$ and $W[\rho]$ are not known exactly and, therefore, approximations are required. A popular approximation is known as the *local density approximation*, which entails deriving expressions for these energies using an ideal electron gas and replacing the dependence of the energy term on the constant density $\rho = N/V$ with the spatially varying density $\rho(\mathbf{r})$. The physical assumption is that, in most systems, the spatial variations of the density are gradual enough that the system locally is well approximated by a constant density and, hence, ideal gas expressions are approximately valid.

II. AN APPROXIMATE KINETIC ENERGY DENSITY FUNCTIONAL

Recall from the last lecture that the total energy of the ideal fermion gas is given by

$$E = \frac{4\pi g V}{5} \left(\frac{m}{2\pi^2 \hbar^2} \right)^{3/2} \varepsilon_F^{5/2}$$

where g is the spin degeneracy, which, for electrons, is 2. Since the Fermi energy is given by

$$\varepsilon_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 \rho}{g} \right)^{2/3}$$

the total energy E becomes

$$E = C_F V \rho^{5/3}$$

where C_F is a collection of constants. The main thing to note here is the dependence of E on the density, i.e. $E \propto \rho^{5/3}$. Since the only energy present in an ideal gas is kinetic energy, E is a kinetic energy T . By dividing by the volume V , we obtain a kinetic energy density t given by

$$t(\rho) = C_F \rho^{5/3}$$

The total kinetic energy is trivially given by integrating both sides over all space:

$$T = \int d\mathbf{r} t(\rho)$$

However, now imagine replacing the constant density ρ in $t(\rho)$ with a spatially varying density $\rho(\mathbf{r})$ in a real electronic system. Then, T becomes a functional of $\rho(\mathbf{r})$ and is given by

$$T[\rho] = \int d\mathbf{r} t(\rho(\mathbf{r})) = C_F \int d\mathbf{r} \rho^{5/3}(\mathbf{r})$$

This is an example of a local density functional.

III. AN EXCHANGE ENERGY DENSITY FUNCTIONAL

In Hartree-Fock theory, the electron-electron repulsion $W[\rho]$ is often written as

$$W[\rho] = \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + E_x[\rho] + E_c[\rho]$$

where E_x and E_c are the exchange and correlation energies, respectively. The first term is just the classical Coulomb energy for two charge densities $\rho(\mathbf{r})$ and $\rho(\mathbf{r}')$, while the exchange and correlation energies contain all of the quantum mechanical information about the electrons. It is possible to obtain a simple closed-form local density expression for the exchange energy using the ideal electron gas.

In Hartree-Fock theory, the exchange energy is given by

$$K = -\frac{e^2}{4} \int d\mathbf{r} d\mathbf{r}' \frac{|\rho_1(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|}$$

where $\rho_1(\mathbf{r}, \mathbf{r}')$ is the one-particle density matrix. For an ideal gas, this density matrix is given by

$$\rho_1(\mathbf{r}, \mathbf{r}') = \sum_m \sum_s \sum_{\mathbf{n}} \langle f_{\mathbf{n}m} \rangle \phi_{\mathbf{n}m}^*(\mathbf{r}, s) \phi_{\mathbf{n}m}(\mathbf{r}', s)$$

where $\phi_{\mathbf{n}m}(\mathbf{r}, s)$ are the single-particle eigenfunctions

$$\phi_{\mathbf{n}m}(\mathbf{r}, s) = \frac{1}{\sqrt{V}} e^{2\pi i \mathbf{n} \cdot \mathbf{r} / L} \chi_m(s)$$

and $\langle f_{\mathbf{n}m} \rangle$ is the zero-temperature average occupation number

$$\langle f_{\mathbf{n}m} \rangle = \theta(\varepsilon_F - \varepsilon_{\mathbf{n}})$$

Substituting in these expressions for the single-particle eigenfunctions and occupation number gives for the density matrix

$$\rho_1(\mathbf{r}, \mathbf{r}') = \sum_m \sum_s \sum_{\mathbf{n}} \theta(\varepsilon_F - \varepsilon_{\mathbf{n}}) e^{-2\pi i \mathbf{n} \cdot \mathbf{r} / L} e^{2\pi i \mathbf{n} \cdot \mathbf{r}' / L} \chi_m^*(s) \chi_m(s)$$

Since $\chi_m(s) = \delta_{ms}$, the spin sum gives

$$\sum_m \sum_s \chi_m^*(s) \chi_m(s) = \sum_m \sum_s \delta_{ms} \delta_{ms} = \sum_m 1 = g$$

where $g = 2$ for electrons. Thus, we obtain for the density matrix

$$\rho_1(\mathbf{r}, \mathbf{r}') = \frac{g}{V} \sum_{\mathbf{n}} \theta(\varepsilon_F - \varepsilon_{\mathbf{n}}) e^{-2\pi i \mathbf{n} \cdot \mathbf{r} / L} e^{2\pi i \mathbf{n} \cdot \mathbf{r}' / L}$$

Taking the thermodynamic limit, turning the sum into an integral, gives

$$\rho_1(\mathbf{r}, \mathbf{r}') = \frac{g}{V} \int d\mathbf{n} \theta(\varepsilon_F - \varepsilon_{\mathbf{n}}) e^{-2\pi i \mathbf{n} \cdot \mathbf{r} / L} e^{2\pi i \mathbf{n} \cdot \mathbf{r}' / L}$$

Defining $\mathbf{s} = \mathbf{r} - \mathbf{r}'$, and choosing the axes of the \mathbf{n} coordinate system such that \mathbf{s} lies along the n_z axis, the integral can be expressed in spherical polar coordinates as

$$\begin{aligned} \rho_1(\mathbf{s}) &= \frac{g}{V} \int_0^{2\pi} d\varphi \int_0^\pi \sin\theta d\theta \int_0^\infty dn n^2 e^{-2\pi i n s \cos\theta / L} \theta(\varepsilon_F - \varepsilon_{\mathbf{n}}) \\ &= \frac{2\pi g}{V} \int_0^\infty dn n^2 \theta(\varepsilon_{\mathbf{n}} - \varepsilon_F) \int_{-1}^1 d(\cos\theta) e^{-2\pi i n s \cos\theta / L} \\ &= \frac{2\pi g}{V} \int_0^\infty dn n^2 \theta(\varepsilon_{\mathbf{n}} - \varepsilon_F) \left[-\frac{L}{2\pi i n s} \left(e^{-2\pi i n s / L} - e^{2\pi i n s / L} \right) \right] \\ &= \frac{2gL}{Vs} \int_0^\infty dn n^2 \theta(\varepsilon_F - \varepsilon_{\mathbf{n}}) \sin(2\pi n s / L) \end{aligned}$$

The step function requires

$$\varepsilon_{\mathbf{n}} \leq \varepsilon_{\text{F}}$$

$$\frac{2\pi^2 \hbar^2}{mL^2} n^2 \leq \varepsilon_{\text{F}}$$

$$n \leq \left(\frac{mL^2}{2\pi^2 \hbar^2} \right)^{1/2} \varepsilon_{\text{F}}^{1/2} \equiv \bar{n}$$

Thus, the density matrix becomes

$$\rho_1(s) = \frac{2gL}{Vs} \int_0^{\bar{n}} dn n \sin(2\pi ns/L) = -\frac{g}{2\pi^2 s} \left[\frac{2\pi\bar{n}}{Ls} \cos(2\pi\bar{n}s/L) - \frac{1}{s^2} \sin(2\pi\bar{n}s/L) \right]$$

Since ρ_1 only depends on $s = |\mathbf{r} - \mathbf{r}'|$, it is useful to introduce the transformation

$$\mathbf{R} = \frac{1}{2}(\mathbf{r} + \mathbf{r}') \quad \mathbf{s} = \mathbf{r} - \mathbf{r}'$$

into the integral for K . The Jacobian of the transformation is 1, hence, the expression for K becomes

$$\begin{aligned} K &= -\frac{g^2 e^2}{16\pi^4} \int d\mathbf{R} ds \frac{1}{s} \left[\frac{2\pi\bar{n}}{Ls} \cos(2\pi\bar{n}s/L) - \frac{1}{s^2} \sin(2\pi\bar{n}s/L) \right]^2 \\ &= -\frac{g^2 e^2 V}{4\pi^3} \int_0^\infty ds \frac{1}{s^5} \left[\frac{2\pi\bar{n}s}{L} \cos(2\pi\bar{n}s/L) - \sin(2\pi\bar{n}s/L) \right]^2 \end{aligned}$$

where, in the last line, the \mathbf{s} integration is written in terms of spherical polar coordinates for \mathbf{s} . Next, we change variables to

$$x = \frac{2\pi\bar{n}s}{L} \quad ds = \frac{L}{2\pi\bar{n}} dx$$

Performing this transformation gives

$$\begin{aligned} K &= -\frac{g^2 e^2 V}{4\pi^3} \left(\frac{2\pi\bar{n}}{L} \right)^4 \int_0^\infty dx \frac{1}{x^5} [x \cos x - \sin x]^2 \\ &= -\frac{4g^2 e^2 \pi \bar{n}^4}{L} \int_0^\infty dx \frac{1}{x^5} [x \cos x - \sin x]^2 \end{aligned}$$

The x integral can be worked out (with much pain) and shown to be just 1/4. Thus, we find the exchange energy is given by

$$\begin{aligned} K &= -\frac{g^2 e^2 \pi \bar{n}^4}{L} \\ &= -\frac{g^2 e^2 \pi}{L} \left(\frac{mL^2}{2\pi^2 \hbar^2} \right)^2 \varepsilon_{\text{F}}^2 \end{aligned}$$

Since $\varepsilon_{\text{F}} \propto \rho^{2/3}$, the exchange energy is proportional to $\rho^{4/3}$. Hence, we can write K in the form

$$K = -e^2 C_x V \rho^{4/3}$$

where C_x is a collection of constants.

Now defining an exchange energy density $e_x(\rho) = K/V$, we find

$$e_x(\rho) = -e^2 C_x \rho^{4/3}$$

Of course, the total exchange energy $K = E_x$ can be obtained trivially by integrating over the containing volume

$$E_x = \int d\mathbf{r} e_x(\rho)$$

However, imagine replacing the constant density $\rho = N/V$ by the spatially varying density $\rho(\mathbf{r})$ for a real electronic system. Then, E_x becomes a functional of the density, given by

$$E_x[\rho] = \int d\mathbf{r} e_x(\rho(\mathbf{r})) = -e^2 C_x \int d\mathbf{r} \rho^{4/3}(\mathbf{r})$$

If the kinetic and exchange energy functionals are combined and E_c is taken to be approximately 0, then we arrive at a well known energy functional

$$E[\rho] = C_F \int d\mathbf{r} \rho^{5/3}(\mathbf{r}) + \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{\rho(\mathbf{r})\rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} - e^2 C_x \int d\mathbf{r} \rho^{4/3}(\mathbf{r}) + \int d\mathbf{r} \rho(\mathbf{r}) V_{\text{ext}}(\mathbf{r})$$

known as the *Thomas-Fermi* functional. Here, $V_{\text{ext}}(\mathbf{r})$ is the external potential, usually taken to be $V_{\text{ext}}(\mathbf{r}) = -Ze/r$, i.e. the Coulomb potential of a nucleus of charge Ze .

The Thomas-Fermi functional was one of the first functionals invented in the early days of density functional theory. By minimizing this functional over all densities subject to the condition that

$$\int d\mathbf{r} \rho(\mathbf{r}) = N$$

where N is the number of electrons, an approximate ground state electronic density can be obtained. While the Thomas-Fermi theory works reasonably well for atoms with large Z , it cannot predict the existence of molecules. Systematic improvements of the functional do somewhat better, however, it was not until the exact formulation of density functional theory by Hohenberg and Kohn that the true power of density functional theory could be realized.