

I. THE DEFINITION OF DENSITY

As we have stressed several times in the lectures, solving the many-particle Schrödinger equation for the ground state wavefunction and energy becomes a daunting task even for the smallest system. An alternative route to the direct solution of the Schrödinger equation is shifting focus of the problem from $\Psi(\vec{r})$ to a fundamental observable of the problem, namely the density $n(\vec{r})$. For a many-particle system the density, $n(\vec{r})$, is found by calculating the expectation value of the single-particle density operator for the many-body wavefunction

$$\hat{n}(\vec{r}) = \sum_{i=1,N} \delta(\vec{r} - \vec{r}_i) \quad (1)$$

$$\begin{aligned} n(\vec{r}) &= \langle \Psi | \hat{n}(\vec{r}) | \Psi \rangle = \sum_{i=1,N} \int \delta(\vec{r} - \vec{r}_i) |\Psi(\vec{r}_1, \dots, \vec{r}_N)|^2 d\vec{r}_1 \dots d\vec{r}_N \\ &= \int |\Psi(\vec{r}, \vec{r}_2, \dots, \vec{r}_N)|^2 d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N + \int |\Psi(\vec{r}_1, \vec{r}, \dots, \vec{r}_N)|^2 d\vec{r}_1 d\vec{r}_3 \dots d\vec{r}_N + \dots \\ &= N \int |\Psi(\vec{r}, \dots, \vec{r}_N)|^2 d\vec{r}_2 \dots d\vec{r}_N \end{aligned} \quad (2)$$

where $\{\vec{r}_i\}$ are the variable associated with each of the electrons. As expected, assuming that the wavefunction is normalized to unity, integrating the electron density over all space yields the number of electrons

$$\int d\vec{r} n(\vec{r}) = N. \quad (3)$$

II. ENERGY IN TERMS OF THE DENSITY

Our goal in density functional theory is to eliminate the wavefunction by writing all terms making up the total ground state energy of the electronic system in terms of density. This is because we would then like to minimize the electronic energy with respect to the density to obtain the ground state energy and the corresponding electronic density. The foundation put forward by Hohenberg and Kohn will be discussed in the next lecture.

As is well-known, once the wavefunction is obtained by solving the Hamiltonian we can determine the observable corresponding to a given operator by calculating the expectation value of that operator. This allows us to separately calculate the energy terms corresponding to the potential operators given in the Hamiltonian that we wrote down in the previous lectures. For the sake of completeness we reproduce the Hamiltonian here once again

$$\begin{aligned} \hat{H}_e &= \hat{T} + \hat{V}_{en} + \hat{V}_{ee} \\ &= -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 - \sum_i^{N_e} \sum_I^{N_n} \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} + \frac{1}{2} \sum_i^{N_e} \sum_{j \neq i}^{N_e} \frac{1}{|\vec{r}_i - \vec{r}_j|} \end{aligned} \quad (4)$$

Suppose now that we have somehow managed to solve the many-body Schrödinger equation and have obtained the wavefunction. The expectation value of the nuclei-electron interaction operator is given by

$$\langle \Psi(\vec{r}_1, \dots, \vec{r}_N) | \hat{V}_{ne} | \Psi(\vec{r}_1, \dots, \vec{r}_N) \rangle = - \sum_i^{N_e} \sum_I^{N_n} \int \Psi^*(\vec{r}_1, \dots, \vec{r}_N) \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} \Psi(\vec{r}_1, \dots, \vec{r}_N) d\vec{r}_1 \dots d\vec{r}_N \quad (5)$$

Since the operator does not contain any derivatives, we may collect the wavefunction and its conjugate under a common norm square

$$\langle \Psi(\vec{r}_1, \dots, \vec{r}_N) | \hat{V}_{ne} | \Psi(\vec{r}_1, \dots, \vec{r}_N) \rangle = - \sum_i^{N_e} \sum_I^{N_n} \int \frac{Z_I}{|\vec{r}_i - \vec{R}_I|} |\Psi(\vec{r}_1, \dots, \vec{r}_N)|^2 d\vec{r}_1 \dots d\vec{r}_N \quad (6)$$

Next, we proceed in a way that is much similar to the one we followed in the calculation of the density. Let's expand the sum over the electronic index i

$$\langle \Psi(\vec{r}_1, \dots, \vec{r}_n) | \hat{V}_{ne} | \Psi(\vec{r}_1, \dots, \vec{r}_n) \rangle = - \sum_I^{N_n} \left[\int \frac{Z_I}{|\vec{r}_1 - \vec{R}_I|} |\Psi(\vec{r}_1, \dots, \vec{r}_N)|^2 d\vec{r}_1 \dots d\vec{r}_N \right. \\ \left. + \int \frac{Z_I}{|\vec{r}_2 - \vec{R}_I|} |\Psi(\vec{r}_1, \dots, \vec{r}_N)|^2 d\vec{r}_1 \dots d\vec{r}_N + \dots \right] \quad (7)$$

For each of the N_e terms in the sum in Eq. 7, we separate the integral over the variable in the Coulombic terms from the others.

$$\langle \Psi(\vec{r}_1, \dots, \vec{r}_n) | \hat{V}_{ne} | \Psi(\vec{r}_1, \dots, \vec{r}_n) \rangle = - \sum_I^{N_n} \left[\int \frac{Z_I}{|\vec{r}_1 - \vec{R}_I|} d\vec{r}_1 \int |\Psi(\vec{r}_1, \dots, \vec{r}_N)|^2 d\vec{r}_2 d\vec{r}_3 \dots d\vec{r}_N \right. \\ \left. + \int \frac{Z_I}{|\vec{r}_2 - \vec{R}_I|} d\vec{r}_2 \int |\Psi(\vec{r}_1, \dots, \vec{r}_N)|^2 d\vec{r}_1 d\vec{r}_3 \dots d\vec{r}_N + \dots \right] \quad (8)$$

For each term in Eq. 8, the second integral is the definition of the density, $n(\vec{r})$ as given in Eq. 2, that is to say Eq. 8 may be written as

$$E_{ne} = \langle \Psi(\vec{r}_1, \dots, \vec{r}_n) | \hat{V}_{ne} | \Psi(\vec{r}_1, \dots, \vec{r}_n) \rangle = - \frac{1}{N_e} \sum_I^{N_n} \left[\int \frac{Z_I}{|\vec{r}_1 - \vec{R}_I|} n(\vec{r}_1) + \int \frac{Z_I}{|\vec{r}_2 - \vec{R}_I|} n(\vec{r}_2) + \dots \right] \quad (9)$$

Since for each term in Eq. 9, an integral over the argument of the density is taken, we may replace these variables by a dummy variable, say vr . Then all the terms become equal and since there are N_e of them the electron-nucleus interaction energy may be written takes the compact form

$$E_{ne} = - \sum_I^{N_n} \int n(\vec{r}) \frac{Z_I}{|\vec{r} - \vec{R}_I|} d\vec{r} = \int n(\vec{r}) V_{ne}(\vec{r}) d\vec{r} \quad (10)$$

This simple linear functional form attained by the electron-nucleus interaction energy is in fact common to all single-body external potential terms such as an applied electric field.

The equivalent derivation for the electron-electron term, however, is not as simple. It can be proven that this term cannot be written in terms of the single-particle density but instead only in terms of the two-particle density

$$E_{ee} = \frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n^{(2)}(\vec{r}, \vec{r}')}{|\vec{r} - \vec{r}'|} \quad (11)$$

where $n^{(2)}$ may be interpreted as the probability that an electron exists at point \vec{r} given that a second electron exists at point \vec{r}' . Eq. 11 may easily be derived in a similar manner to E_{ne} . It is this term that makes the many-particle problem so hard to solve. If we knew this pairwise conditional probability, then we would be able to solve the problem exactly. However, the method that we are about to develop does not allow for the existence of such a two-particle density but instead only the one-particle density. That being the case, we are forced to make an approximation. Now, if the two electrons were completely *uncorrelated* then the two-particle density in Eq. 11 would just be the product of one-particle densities (we may also make the same statement about probabilities). Here, we write $n^{(2)}$ in terms of this product plus a correction

$$n^{(2)}(\vec{r}, \vec{r}') = n(\vec{r})n(\vec{r}') + \Delta n^{(2)}(\vec{r}, \vec{r}') \quad (12)$$

The electron-electron energy of Eq. 11 may then be written as

$$E_{ee} = \frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n(\vec{r})n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \Delta E_{ee} \quad (13)$$

where the second term obviously comes from the correction in Eq. 12.

The kinetic energy poses an even larger problem. Since the kinetic energy operator contains a derivative term, there's no way we can write it in terms of the density since it is impossible to collect the wavefunction and its conjugate as a single norm square.

$$T = - \frac{1}{2} \int d\vec{r} \Psi^*(\vec{r}_1, \dots, \vec{r}_n) \nabla^2 \Psi(\vec{r}_1, \dots, \vec{r}_n) \quad (14)$$

In order to tackle the kinetic energy, we make one of the key assumptions of density functional theory. We assume that the density can be written as the sum norm squares of a collection of single-particle orbitals

$$n(\vec{r}) = \sum_n^{N_e} |\phi_n(\vec{r})|^2 \quad (15)$$

These orbitals are called *Kohn-Sham* orbitals and they are initially completely unspecified in much the same way as in the orbitals in the Slater determinant in the Hartree-Fock formalism. The above form cannot really be considered an approximation. It simply says that instead of the full many-particle system we consider an auxiliary system of single-particle orbitals that have the same ground state density as the real system. Whether such an auxiliary system can be found for every real system is a topic of debate but if it can be found the treatment remains exact.

Writing the density as we have in Eq. 15 suggests that we write the kinetic energy as the sum of the kinetic energies of the Kohn-Sham orbitals. However, this of course is not going to equal the kinetic energy of the real many-particle system. Once again then we express the kinetic energy as the single-particle kinetic energy plus a correction

$$T = -\frac{1}{2} \sum_n^{N_e} \int d\vec{r} \phi_n^*(\vec{r}) \nabla^2 \phi_n(\vec{r}) d\vec{r} + \Delta T \quad (16)$$

Finally putting together everything, the total ground state energy may be written as

$$E = -\frac{1}{2} \sum_n^{N_e} \int d\vec{r} \phi_n^*(\vec{r}) \nabla^2 \phi_n(\vec{r}) d\vec{r} + \int n(\vec{r}) V_{ne}(\vec{r}) d\vec{r} + \frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \Delta T + \Delta E_{ee} \quad (17)$$

The kinetic energy as written cannot be differentiated directly with respect to $n(\vec{r})$ but it can be minimized with respect to the orbitals which is equivalent to minimizing with respect to $n(\vec{r})$.

Now the only thing that remains to be done is to write the last two (correction) terms in terms of the density as well. In density functional theory, these additional terms, δE_{ee} and ΔE_K play a crucial role. So far, our conversion of the energy from the wavefunction representation to the density representation has been exact. From this point forward, we will rely on the accuracy of certain approximations to the sum of these two terms, called the *exchange-correlation* energy.

$$E_{xc} = \Delta E_{ee} + \Delta T \quad (18)$$

The origin of this term is the difference between a system of N interacting and noninteracting particles. More specifically, the origin of

- exchange energy is the Pauli repulsion, omitted in the Hartree term.
- correlation energy is the repulsion between electrons.

Several well-developed approximations to this sum exists but here we shall only consider the local approximation given by

$$E_{xc} = \int d\vec{r} n(\vec{r}) \epsilon_{xc}(n) \quad (19)$$

where $\epsilon_{xc}(n)$ is a simple function of n . We will see more on exchange-correlation functionals later. Thus, within this approximation, the total energy may be written as

$$E = -\frac{1}{2} \sum_n^{N_e} \int d\vec{r} \phi_n^*(\vec{r}) \nabla^2 \phi_n(\vec{r}) d\vec{r} + \int n(\vec{r}) V_{ne}(\vec{r}) d\vec{r} + \frac{1}{2} \int \int d\vec{r} d\vec{r}' \frac{n(\vec{r}) n(\vec{r}')}{|\vec{r} - \vec{r}'|} + \int d\vec{r} \epsilon_{xc}(n) n(\vec{r}). \quad (20)$$

We'll use this result first to prove the most important theorems (by Hohenberg and Kohn) on DFT and later to use functional derivatives to obtain the Kohn-Sham system of equations which make DFT possible in practice.