Proof that the Electron Density for a Set of Indistinguishable Independent Particles is Given by

$$n(\mathbf{r}) = \sum_{\text{occ } i} \left|\psi_i(\mathbf{r})\right|^2 .$$

Step 1. The Many-Body Wavefunction as a Slater Determinant

For a system of N indistinguishable independent particles, the many-body wavefunction can be written as a Slater determinant:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \cdots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \cdots & \psi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \cdots & \psi_N(\mathbf{r}_N) \end{vmatrix} .$$

Here, the functions $\psi_i(\mathbf{r})$ are the orthonormal single-particle orbitals occupied in the system.

Step 2. Definition of the One-Particle Density

The electron density $n(\mathbf{r})$ is defined as the probability density of finding any one electron at position $\mathbf{r}$. In a system with N particles, it is given by:

$$n(\mathbf{r}) = N \int |\Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N)|^2 \, d\mathbf{r}_2 \cdots d\mathbf{r}_N .$$

Step 3. Expressing the Density in Terms of the One-Particle Density Matrix

For a Slater determinant wavefunction, it is a standard result that the one-body (or reduced) density matrix is:

$$\rho(\mathbf{r}, \mathbf{r}') = \sum_{i=1}^{N} \psi_i(\mathbf{r}) \, \psi_i^*(\mathbf{r}') .$$

The electron density is obtained by taking the diagonal element of this density matrix:

$$n(\mathbf{r}) = \rho(\mathbf{r}, \mathbf{r}) = \sum_{i=1}^{N} \psi_i(\mathbf{r}) \, \psi_i^*(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2 .$$

Conclusion

Thus, for a set of indistinguishable independent particles (i.e., a system described by a Slater determinant), the electron density is given by

$$\boxed{n(\mathbf{r}) = \sum_{\text{occ } i} \left|\psi_i(\mathbf{r})\right|^2 .}$$

This completes the proof.

Legendre Transformation in Density Functional Theory

In thermodynamics and classical mechanics, a Legendre transformation is used to switch from one set of independent variables to their conjugate variables. For example, one may transform the internal energy $U(S, V)$ (a function of entropy S and volume V) into the Helmholtz free energy $F(T, V)$ (a function of temperature T and volume V).

1. The Starting Point: Energy as a Functional of the External Potential

In Density Functional Theory (DFT), the ground-state energy of an interacting many-electron system is originally expressed as a functional of the external potential $v_{\text{ext}}(\mathbf{r})$. That is,

$$E[v_{\text{ext}}] = \langle \Psi[v_{\text{ext}}] \mid \hat{H}[v_{\text{ext}}] \mid \Psi[v_{\text{ext}}] \rangle,$$

where the Hamiltonian is given by

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{r}_i).$$

In this formulation, the energy E depends on the entire function $v_{\text{ext}}(\mathbf{r})$.

2. Conjugate Variables: External Potential and Electron Density

A central result in DFT is that the ground-state electron density $n(\mathbf{r})$ is given by the functional derivative of the energy with respect to the external potential:

$$n(\mathbf{r}) = \frac{\delta E[v_{\text{ext}}]}{\delta v_{\text{ext}}(\mathbf{r})}.$$

This relation shows that $n(\mathbf{r})$ and $v_{\text{ext}}(\mathbf{r})$ are conjugate variables, much like entropy and temperature are conjugate in thermodynamics.

Conjugate Variables and Functional Derivatives

A key insight in DFT is that the external potential $v_{\text{ext}}(\mathbf{r})$ and the electron density $n(\mathbf{r})$ are conjugate variables. This means that the electron density is obtained by taking the functional derivative of the energy with respect to $v_{\text{ext}}(\mathbf{r})$:

$$n(\mathbf{r}) = \frac{\delta E[v_{\text{ext}}]}{\delta v_{\text{ext}}(\mathbf{r})}.$$

In simple terms, this tells us that if we make a small change in the external potential at the point $\mathbf{r}$, the corresponding change in the energy is proportional to the electron density at that point.

Role of the Hellmann–Feynman Theorem

The Hellmann–Feynman theorem provides further justification. If the Hamiltonian $\hat{H}(\lambda)$ depends on a parameter λ, then the theorem states that

$$\frac{dE}{d\lambda} = \left\langle \Psi(\lambda) \left| \frac{\partial \hat{H}(\lambda)}{\partial \lambda} \right| \Psi(\lambda) \right\rangle .$$

Here, if we think of a variation in the external potential at a point $\mathbf{r}$ as a change in a parameter λ, we have

$$\frac{\delta E[v_{\text{ext}}]}{\delta v_{\text{ext}}(\mathbf{r})} = \left\langle \Psi \left| \frac{\delta \hat{H}}{\delta v_{\text{ext}}(\mathbf{r})} \right| \Psi \right\rangle .$$

Since the external potential enters the Hamiltonian as

$$\hat{V} = \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{r}_i),$$

its functional derivative with respect to $v_{\text{ext}}(\mathbf{r})$ is

$$\frac{\delta \hat{V}}{\delta v_{\text{ext}}(\mathbf{r})} = \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i).$$

Taking the expectation value of this operator yields

$$\frac{\delta E[v_{\text{ext}}]}{\delta v_{\text{ext}}(\mathbf{r})} = \langle \Psi | \sum_{i=1}^{N} \delta(\mathbf{r} - \mathbf{r}_i) | \Psi \rangle,$$

which is precisely the definition of the electron density $n(\mathbf{r})$.

3. Performing the Legendre Transformation

Because $v_{\text{ext}}(\mathbf{r})$ and $n(\mathbf{r})$ are conjugate, we can perform a Legendre transformation to change the independent variable from $v_{\text{ext}}(\mathbf{r})$ to $n(\mathbf{r})$. This leads to the energy functional expressed as a functional of the density:

$$E_{\text{HK}}[n] = F_{\text{HK}}[n] + \int d\mathbf{r}\; v_{\text{ext}}(\mathbf{r})\, n(\mathbf{r})\, ,$$

where

$$F_{\text{HK}}[n] = \langle \hat{T} \rangle + \langle \hat{V}_{ee} \rangle$$

is the universal functional—independent of the external potential—and represents the kinetic and electron-electron interaction energies.

4. Invertibility and One-to-One Correspondence

The Legendre transformation is only possible if the mapping from $v_{\text{ext}}(\mathbf{r})$ to $n(\mathbf{r})$ is invertible. The Hohenberg–Kohn theorem guarantees that for a nondegenerate ground state, there is a one-to-one correspondence (up to an additive constant) between the external potential $v_{\text{ext}}(\mathbf{r})$ and the ground-state density $n(\mathbf{r})$. This invertibility means that once the density is known, the external potential (and therefore the entire Hamiltonian) is determined, allowing us to recast the ground-state energy purely as a functional of $n(\mathbf{r})$.

5. Implications

The Legendre transformation in DFT has several important implications:

- **Universality:** The universal functional $F_{\text{HK}}[n]$ is the same for all electronic systems, independent of the external potential.
- **General Applicability:** Although the ground-state energy originally depends on $v_{\text{ext}}(\mathbf{r})$, the Legendre transformation shows that the same formalism applies to any external potential. That is, the energy can be defined as a functional of $n(\mathbf{r})$ for a *range* of potentials, not just one particular potential.
- **Reduction in Complexity:** Instead of dealing with a complex many-body wavefunction (or the external potential as a function over 3-dimensional space), we work with the electron density $n(\mathbf{r})$, which is also a function in three-dimensional space. This dramatically simplifies the problem.

What Does It Mean for a Potential to be *Local*?

A potential is said to be *local* if it acts multiplicatively in the position (coordinate) representation. This means that, when expressed in the coordinate basis, the potential operator does not mix different positions; instead, it acts directly by multiplication by a function of position.

For example, consider a one-particle potential $v(\mathbf{r})$. In the coordinate representation, its action on a wave function $\psi(\mathbf{r})$ is given by:

$$[\hat{v}\psi](\mathbf{r}) = v(\mathbf{r})\,\psi(\mathbf{r}).$$

Notice that the operator $\hat{v}$ is diagonal in the coordinate basis.

In the context of many-body systems, if the potential energy operator for N particles can be written as

$$\hat{V} = \sum_{i=1}^{N} v(\mathbf{r}_i),$$

then each term $v(\mathbf{r}_i)$ depends only on the position of the ith particle. When this operator acts on a many-body wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$, we have:

$$[\hat{V}\Psi](\mathbf{r}_1, \ldots, \mathbf{r}_N) = \sum_{i=1}^{N} v(\mathbf{r}_i)\,\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N).$$

This separability into a sum of one-particle potentials is what is meant by the potential being *local.*

In contrast, a *non-local* potential does not act solely by multiplication at a single point. Instead, it may involve an integral operator that couples the wave function at different points. For instance, a non-local potential might be written as:

$$[\hat{V}\psi](\mathbf{r}) = \int d\mathbf{r}'\,V(\mathbf{r}, \mathbf{r}')\,\psi(\mathbf{r}'),$$

where the value at $\mathbf{r}$ depends on $\psi(\mathbf{r}')$ for other values of $\mathbf{r}'$.

Proof

We wish to prove that for a general many-particle wave function

$$\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

and a local potential energy operator (which is multiplicative in the local representation)

$$\hat{V} = \sum_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i)\,,$$

where $V_{\text{ext}}(\mathbf{r})$ is a function of position in 3D and N is the number of particles, the expectation value of $\hat{V}$ is given by

$$\langle \Psi | \hat{V} | \Psi \rangle = \int d^3r\, n(\mathbf{r})\, V_{\text{ext}}(\mathbf{r})\,.$$

Here, $n(\mathbf{r})$ is the one-particle density.

Proof:

1. Definition of the One-Particle Density

For a normalized many-particle wave function $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$, the one-particle density is defined as

$$n(\mathbf{r}) = N \int d^3r_2\, d^3r_3 \cdots d^3r_N \left| \Psi(\mathbf{r}, \mathbf{r}_2, \ldots, \mathbf{r}_N) \right|^2 .$$

2. Expression for the Expectation Value

The expectation value of the operator $\hat{V}$ is

$$\langle \Psi | \hat{V} | \Psi \rangle = \int d^3r_1 \cdots d^3r_N\, \Psi^*(\mathbf{r}_1, \ldots, \mathbf{r}_N) \left(\sum_{i=1}^{N} V_{\text{ext}}(\mathbf{r}_i) \right) \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)\,.$$

3. Interchanging Sum and Integration

Since the sum over i is finite, we may interchange the sum and the integrals:

$$\langle \Psi | \hat{V} | \Psi \rangle = \sum_{i=1}^{N} \int d^3r_1 \cdots d^3r_N\, V_{\text{ext}}(\mathbf{r}_i) \left| \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \right|^2 .$$

For a fixed index i, denote

$$I_i = \int d^3r_1 \cdots d^3r_N\, V_{\text{ext}}(\mathbf{r}_i) \left| \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \right|^2 .$$

4. Using the Symmetry of the Wave Function

Because Ψ is (anti-)symmetric with respect to the interchange of particle coordinates, each term I_i is identical. Without loss of generality, consider $i = 1$:

$$I_1 = \int d^3r_1\, V_{\text{ext}}(\mathbf{r}_1) \left[\int d^3r_2 \cdots d^3r_N \left| \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) \right|^2 \right] .$$

By the definition of $n(\mathbf{r})$, we have

$$\int d^3r_2 \cdots d^3r_N \left| \Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N) \right|^2 = \frac{1}{N}\, n(\mathbf{r}_1)\,.$$

Thus,

$$I_1 = \frac{1}{N} \int d^3 r_1 \, V_{\text{ext}}(\mathbf{r}_1) \, n(\mathbf{r}_1) \, .$$

5. Summing Over All Particles

Since all I_i are equal,

$$\langle \Psi | \hat{V} | \Psi \rangle = \sum_{i=1}^{N} I_i = N \cdot \frac{1}{N} \int d^3 r \, V_{\text{ext}}(\mathbf{r}) \, n(\mathbf{r}) = \int d^3 r \, V_{\text{ext}}(\mathbf{r}) \, n(\mathbf{r}) \, .$$

Thus, we have shown that

$$\boxed{\langle \Psi | \hat{V} | \Psi \rangle = \int d^3 r \, n(\mathbf{r}) \, V_{\text{ext}}(\mathbf{r}) \, .}$$

v-Representability in the Hohenberg–Kohn Theorems

In Density Functional Theory (DFT), one of the central ideas is that the ground-state properties of an interacting many-electron system can be uniquely determined by its electron density $n(\mathbf{r})$. The original Hohenberg–Kohn (HK) theorems establish a one-to-one correspondence between the ground-state density and the external potential $v_{\text{ext}}(\mathbf{r})$ (up to an additive constant). However, a key assumption in their proofs is that the densities under consideration are *v-representable.*

Definition of v-Representability

A density $n(\mathbf{r})$ is said to be *v-representable* if there exists some local external potential $v_{\text{ext}}(\mathbf{r})$ for which $n(\mathbf{r})$ is the ground-state density of the Hamiltonian

$$\hat{H} = \hat{T} + \hat{V}_{ee} + \sum_{i=1}^{N} v_{\text{ext}}(\mathbf{r}_i)\,.$$

That is, $n(\mathbf{r})$ is v-representable if it can be obtained as the solution (i.e., the ground-state density) of the Schrödinger equation for some local potential $v_{\text{ext}}(\mathbf{r})$.

Importance in the Hohenberg–Kohn Theorems

The v-representability condition is crucial in the original HK proofs for two main reasons:

- **One-to-One Mapping:** The HK theorems rely on the assumption that the density $n(\mathbf{r})$ comes from some local potential. Under this assumption, they prove that if two different external potentials yield the same ground-state density, then the potentials can differ only by an additive constant. This one-to-one correspondence between $v_{\text{ext}}(\mathbf{r})$ and $n(\mathbf{r})$ is fundamental to formulating DFT.
- **Variational Principle:** The ground-state energy is expressed as a functional of the density,

$$E[n] = F[n] + \int d\mathbf{r}\, v_{\text{ext}}(\mathbf{r})\, n(\mathbf{r})\,,$$

and the proof that the minimum of $E[n]$ equals the true ground-state energy E_{GS} relies on restricting the domain of $n(\mathbf{r})$ to those densities that are v-representable.

Limitations and Later Developments

Not every mathematically acceptable density (i.e., any nonnegative function that integrates to the correct number of electrons) is v-representable. There may exist densities that cannot be obtained as the ground-state density for any local potential. Consequently, the original HK proofs apply only to the subset of densities that are v-representable.

Later developments, such as the constrained search formulation by Levy and Lieb, relax this restriction by considering the broader concept of N-*representability*—requiring only that the density originates from some antisymmetric N-electron wavefunction, regardless of whether it is produced by a local potential. This generalization makes the theory more practical and applicable to a wider range of systems.