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# Chapter 8

# Hartree-Fock and Density Functional Theories

## 8.1 Second Quantization

### 8.1.1 Basis states and creation/annihilation operators

Second quantization is a convenient scheme to label basis states of a many particle quantum system. We are ultimately interested in solutions of the many-body Schrödinger equation,

$$\hat{H}\Psi(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) = E\,\Psi(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) \tag{8.1}$$

where the Hamiltonian is

$$\hat{H} = \sum_{i=1}^{N}\left(-\frac{\hbar^2}{2m}\boldsymbol{\nabla}_i^2 + v_{\text{ext}}(\boldsymbol{x}_i)\right) + \sum_{j<k}^{N} u(\boldsymbol{x}_j - \boldsymbol{x}_k)$$

$$\equiv \hat{T} + \hat{U} + \hat{V} \quad, \tag{8.2}$$

where $\hat{T}$ is the kinetic energy, $\hat{U}$ the one-body potential energy, and $\hat{V}$ the two-body potential energy. To the coordinate labels $\{\boldsymbol{x}_1,\ldots\boldsymbol{x}_N\}$ we may also append labels for internal degrees of freedom, such as spin polarization, denoted $\{\sigma_1,\ldots,\sigma_N\}$. Since $\left[\hat{H},\pi\right]=0$ for all permutations $\pi \in \mathcal{S}_N$, the many-body wavefunctions may be chosen to transform according to irreducible representations of the symmetric group $\mathcal{S}_N$. Thus, for any $\pi \in \mathcal{S}_N$,

$$\Psi\big(\boldsymbol{x}_{\pi(1)},\ldots,\boldsymbol{x}_{\pi(N)}\big) = \left\{ \begin{matrix} 1 \\ \text{sgn}(\pi) \end{matrix} \right\} \Psi(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N) \quad, \tag{8.3}$$

where the upper choice is for Bose-Einstein statistics and the lower sign for Fermi-Dirac statistics. Here $\boldsymbol{x}_j$ may include not only the spatial coordinates of particle $j$, but its internal quantum number(s) as well, such as the spin polarization $\sigma_j$.

A convenient basis for the many body states is obtained from the single-particle eigenstates $\{|\alpha\rangle\}$ of some single-particle Hamiltonian $\hat{H}_0$, with $\langle x | \alpha \rangle = \varphi_\alpha(x)$ and $\hat{H}_0 | \alpha \rangle = \varepsilon_\alpha | \alpha \rangle$. The basis may be taken as orthonormal, *i.e.* $\langle \alpha | \alpha' \rangle = \delta_{\alpha\alpha'}$. Now define

$$\Psi_{\{\alpha_1,\ldots,\alpha_N\}}(x_1,\ldots,x_N) = \frac{1}{\sqrt{N! \prod_\alpha n_\alpha!}} \sum_{\pi \in \mathcal{S}_N} \left\{ \begin{array}{c} 1 \\ \mathsf{sgn}(\pi) \end{array} \right\} \varphi_{\alpha_{\pi(1)}}(x_1) \cdots \varphi_{\alpha_{\pi(N)}}(x_N) \quad . \tag{8.4}$$

These states form a basis for the $N$-particle Hilbert space. Here $n_\alpha$ is the number of times the index $\alpha$ appears among the set $\{\alpha_1,\ldots,\alpha_N\}$. For BE statistics, $n_\alpha \in \{0,1,2,\ldots\}$, whereas for FD statistics, $n_\alpha \in \{0,1\}$. Note that the above states are normalized[1]:

$$\int d^d x_1 \cdots \int d^d x_N \left| \Psi_{\{\alpha_1,\ldots,\alpha_N\}}(x_1,\ldots,x_N) \right|^2 = \frac{1}{N! \prod_\alpha n_\alpha!} \sum_{\pi,\mu \in \mathcal{S}_N} \left\{ \begin{array}{c} 1 \\ \mathsf{sgn}(\pi\mu) \end{array} \right\} \prod_{j=1}^N \int d^d x_j \, \varphi^*_{\alpha_{\pi(j)}}(x_j) \, \varphi_{\alpha_{\mu(j)}}(x_j)$$

$$= \frac{1}{\prod_\alpha n_\alpha!} \sum_{\pi \in \mathcal{S}_N} \prod_{j=1}^N \delta_{\alpha_j, \alpha_{\pi(j)}} = 1 \quad . \tag{8.5}$$

Note that

$$\sum_{\pi \in \mathcal{S}_N} \varphi_{\alpha_{\pi(1)}}(x_1) \cdots \varphi_{\alpha_{\pi(N)}}(x_N) \equiv \mathsf{per}\{\varphi_{\alpha_i}(x_j)\}$$

$$\sum_{\pi \in \mathcal{S}_N} \mathsf{sgn}(\pi) \, \varphi_{\alpha_{\pi(1)}}(x_1) \cdots \varphi_{\alpha_{\pi(N)}}(x_N) \equiv \mathsf{det}\{\varphi_{\alpha_i}(x_j)\} \quad , \tag{8.6}$$

which stand for *permanent* and *determinant*, respectively. We may now write

$$\Psi_{\{\alpha_1,\ldots,\alpha_N\}}(x_1,\ldots,x_N) = \langle x_1, \ldots, x_N | \alpha_1 \cdots \alpha_N \rangle \quad , \tag{8.7}$$

where

$$| \alpha_1 \cdots \alpha_N \rangle = \frac{1}{\sqrt{N! \prod_\alpha n_\alpha!}} \sum_{\pi \in \mathcal{S}_N} \left\{ \begin{array}{c} 1 \\ \mathsf{sgn}(\pi) \end{array} \right\} | \alpha_{\pi(1)} \rangle \otimes | \alpha_{\pi(2)} \rangle \otimes \cdots \otimes | \alpha_{\pi(N)} \rangle \quad . \tag{8.8}$$

Note that $| \alpha_{\pi(1)} \cdots \alpha_{\pi(N)} \rangle = (\pm 1)^\pi | \alpha_1 \cdots \alpha_N \rangle$, where by $(\pm 1)^\pi$ we mean $1$ in the case of BE statistics and $\mathsf{sgn}(\pi)$ in the case of FD statistics.

We may express $| \alpha_1 \cdots \alpha_N \rangle$ as a product of creation operators acting on a vacuum $| 0 \rangle$ in *Fock space*. For bosons,

$$| \alpha_1 \cdots \alpha_N \rangle = \prod_\alpha \frac{(b_\alpha^\dagger)^{n_\alpha}}{\sqrt{n_\alpha!}} | 0 \rangle \equiv | \{n_\alpha\} \rangle \quad , \tag{8.9}$$

---

[1] In the normalization integrals, each $\int d^d x$ implicitly includes a sum $\sum_\zeta$ over any internal indices that may be present.

where $n_\alpha$ is the multiplicity of the label $\alpha$ in the set $\{\alpha_1, \ldots, \alpha_N\}$. Consequently, $N = \sum_\alpha n_\alpha$. The Hermitian conjugate of the creation operator $b_\alpha^\dagger$ is the annihilation operator $b_\alpha$. The relations among these operators are

$$[b_\alpha, b_\beta] = 0 \quad , \quad [b_\alpha^\dagger, b_\beta^\dagger] = 0 \quad , \quad [b_\alpha, b_\beta^\dagger] = \delta_{\alpha\beta} \quad , \tag{8.10}$$

where $[\bullet, \bullet]$ is the commutator.

For fermions,

$$|\alpha_1 \cdots \alpha_N\rangle = \prod_\alpha (c_\alpha^\dagger)^{n_\alpha} |0\rangle = c_{\alpha_1}^\dagger c_{\alpha_2}^\dagger \cdots c_{\alpha_N}^\dagger |0\rangle \equiv |\{n_\alpha\}\rangle \quad , \tag{8.11}$$

where each $n_\alpha \in \{0, 1\}$ and where $\sum_\alpha n_\alpha = N$. Thus $n_\alpha = 1$ for each $\alpha \in \{\alpha_1, \ldots, \alpha_N\}$ and $n_\alpha = 0$ otherwise. We also implicitly assume a canonical, though arbitrary, ordering of the single particle labels $\alpha$. The fermionic creation and annihilation operators satisfy the relations

$$\{c_\alpha, c_\beta\} = 0 \quad , \quad \{c_\alpha^\dagger, c_\beta^\dagger\} = 0 \quad , \quad \{c_\alpha, c_\beta^\dagger\} = \delta_{\alpha\beta} \quad , \tag{8.12}$$

where $\{\bullet, \bullet\}$ is the anticommutator. Because the fermion creation operators all anticommute, we have

$$c_{\alpha_{\pi(1)}}^\dagger c_{\alpha_{\pi(2)}}^\dagger \cdots c_{\alpha_{\pi(N)}}^\dagger |0\rangle = \mathsf{sgn}(\pi) |\{n_\alpha\}\rangle \quad , \tag{8.13}$$

for any $\pi \in \mathcal{S}_N$.

We may also define the operators

$$b(\boldsymbol{x}) = \sum_\alpha \varphi_\alpha(\boldsymbol{x})\, b_\alpha \quad , \quad c(\boldsymbol{x}) = \sum_\alpha \varphi_\alpha(\boldsymbol{x})\, c_\alpha \quad , \tag{8.14}$$

which satisfy

$$[b(\boldsymbol{x}), b^\dagger(\boldsymbol{x}')] = \delta(\boldsymbol{x} - \boldsymbol{x}') \quad , \quad \{c(\boldsymbol{x}), c^\dagger(\boldsymbol{x}')\} = \delta(\boldsymbol{x} - \boldsymbol{x}') \quad . \tag{8.15}$$

In cases where there are internal (*e.g.*, spin) degrees of freedom, the above relations become

$$[b_m(\boldsymbol{x}), b_{m'}^\dagger(\boldsymbol{x}')] = \delta(\boldsymbol{x} - \boldsymbol{x}')\, \delta_{mm'} \quad , \quad \{c_m(\boldsymbol{x}), c_{m'}^\dagger(\boldsymbol{x}')\} = \delta(\boldsymbol{x} - \boldsymbol{x}')\, \delta_{mm'} \quad . \tag{8.16}$$

In other words,

$$b_{\alpha,m} = \int d^d x\, \varphi_\alpha^*(\boldsymbol{x}, m)\, b_m(\boldsymbol{x}) \quad , \quad c_{\alpha,m} = \int d^d x\, \varphi_\alpha^*(\boldsymbol{x}, m)\, c_m(\boldsymbol{x}) \quad . \tag{8.17}$$

Note the difference between the many-body states

$$|\boldsymbol{x}_1 \cdots \boldsymbol{x}_N\rangle \equiv \psi^\dagger(\boldsymbol{x}_1) \cdots \psi^\dagger(\boldsymbol{x}_N) |0\rangle$$
$$= \frac{1}{\sqrt{N!}} \sum_{\pi \in \mathcal{S}_N} \left\{ \begin{matrix} 1 \\ \mathsf{sgn}(\pi) \end{matrix} \right\} |\boldsymbol{x}_{\pi(1)}, \ldots, \boldsymbol{x}_{\pi(N)}\rangle \tag{8.18}$$

and

$$| \, \boldsymbol{x}_1 \, , \, \ldots \, , \, \boldsymbol{x}_N \, \rangle = | \, \boldsymbol{x}_1 \, \rangle \otimes \cdots \otimes | \, \boldsymbol{x}_N \, \rangle \quad . \tag{8.19}$$

In particular,

$$\langle \, \boldsymbol{x}_1 \, , \, \ldots \, , \, \boldsymbol{x}_N \, | \, \alpha_1 \cdots \alpha_N \, \rangle = \Psi_{\{\alpha_1, \ldots, \alpha_N\}}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) \tag{8.20}$$

but

$$\langle \, \boldsymbol{x}_1 \cdots \boldsymbol{x}_N \, | \, \alpha_1 \cdots \alpha_N \, \rangle = \sqrt{N!} \, \Psi_{\{\alpha_1, \ldots, \alpha_N\}}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) \quad . \tag{8.21}$$

A general normalized $N$-body wavefunction $\Psi_{m_1, \ldots, m_N}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$ may be expressed in second quantized notation as

$$| \, \Psi \, \rangle = \frac{1}{\sqrt{N!}} \sum_{m_1} \cdots \sum_{m_N} \int d^d x_1 \cdots \int d^d x_N \, \Psi_{m_1, \ldots, m_N}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) \, \psi_{m_1}^\dagger(\boldsymbol{x}_1) \cdots \psi_{m_N}^\dagger(\boldsymbol{x}_N) | \, 0 \, \rangle \tag{8.22}$$

where $\psi_m^\dagger(\boldsymbol{x})$ is the bosonic or fermionic creation operator for particles of internal index $m$ at position $\boldsymbol{x}$. Dropping for the moment the internal indices for the sake of simplicity, note that

$$\langle \, 0 \, | \, \psi(\boldsymbol{y}_2) \, \psi(\boldsymbol{y}_1) \, \psi^\dagger(\boldsymbol{x}_1) \, \psi^\dagger(\boldsymbol{x}_2) \, | \, 0 \, \rangle = \langle \, 0 \, | \, \psi(\boldsymbol{y}_2) \, \psi^\dagger(\boldsymbol{x}_2) \, | \, 0 \, \rangle \, \delta(\boldsymbol{x}_1 - \boldsymbol{y}_1)$$
$$\pm \langle \, 0 \, | \, \psi(\boldsymbol{y}_2) \, \psi(\boldsymbol{x}_1) \, \psi^\dagger(\boldsymbol{y}_1) \, \psi^\dagger(\boldsymbol{x}_2) \, | \, 0 \, \rangle \tag{8.23}$$
$$= \delta(\boldsymbol{x}_1 - \boldsymbol{y}_1) \, \delta(\boldsymbol{x}_2 - \boldsymbol{y}_2) \pm \delta(\boldsymbol{x}_1 - \boldsymbol{y}_2) \, \delta(\boldsymbol{x}_2 - \boldsymbol{y}_1) \quad .$$

Reasoning thusly, we conclude that

$$\langle \, 0 \, | \, \psi(\boldsymbol{y}_N) \cdots \psi(\boldsymbol{y}_1) \, \psi^\dagger(\boldsymbol{x}_1) \cdots \psi^\dagger(\boldsymbol{x}_N) \, | \, 0 \, \rangle = \sum_{\sigma \in \mathcal{S}_N} \left\{ \begin{matrix} 1 \\ \mathrm{sgn}(\pi) \end{matrix} \right\} \prod_{j=1}^N \delta(\boldsymbol{y}_j - \boldsymbol{x}_{\sigma(j)}) \quad . \tag{8.24}$$

Including the internal indices, then,

$$\langle \, 0 \, | \, \psi(\boldsymbol{y}_N)_{n_N} \cdots \psi_{n_1}(\boldsymbol{y}_1) \, \psi_{m_1}^\dagger(\boldsymbol{x}_1) \cdots \psi_{m_N}^\dagger(\boldsymbol{x}_N) \, | \, 0 \, \rangle = \sum_{\sigma \in \mathcal{S}_N} \left\{ \begin{matrix} 1 \\ \mathrm{sgn}(\pi) \end{matrix} \right\} \prod_{j=1}^N \delta(\boldsymbol{y}_j - \boldsymbol{x}_{\sigma(j)}) \, \delta_{n_j, m_{\sigma(j)}} \quad . \tag{8.25}$$

We then have

$$\langle \, \Phi \, | \, \Psi \, \rangle = \sum_{m_1} \cdots \sum_{m_N} \int d^d x_1 \cdots \int d^d x_N \, \Phi_{m_1, \ldots, m_N}^*(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) \, \Psi_{m_1, \ldots, m_N}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) \tag{8.26}$$

Another useful thing to derive are expressions for the one- and two-body density matrices. Note that (with internal indices once again suppressed)

$$\psi(\boldsymbol{x}) \, \psi^\dagger(\boldsymbol{x}_1) \cdots \psi^\dagger(\boldsymbol{x}_N) = \delta(\boldsymbol{x} - \boldsymbol{x}_1) \, \psi^\dagger(\boldsymbol{x}_2) \cdots \psi^\dagger(\boldsymbol{x}_N) \pm \delta(\boldsymbol{x} - \boldsymbol{x}_2) \, \psi^\dagger(\boldsymbol{x}_1) \, \psi^\dagger(\boldsymbol{x}_3) \cdots \psi^\dagger(\boldsymbol{x}_N)$$
$$+ \ldots + (\pm 1)^{N-1} \, \delta(\boldsymbol{x} - \boldsymbol{x}_N) \, \psi^\dagger(\boldsymbol{x}_1) \cdots \psi^\dagger(\boldsymbol{x}_{N-1}) \quad , \tag{8.27}$$

from which we may derive the one-body density matrix,

$$
\begin{aligned}
n_1(\boldsymbol{x}\,|\,\boldsymbol{y}) &\equiv \langle\,\Psi\,|\,\psi^\dagger(\boldsymbol{y})\,\psi(\boldsymbol{x})\,|\,\Psi\,\rangle \\
&= N\int d^dx_2\cdots\int d^dx_N\,\Psi^*(\boldsymbol{y},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)\,\Psi(\boldsymbol{x},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)\quad.
\end{aligned}
\tag{8.28}
$$

Similarly, the two-body density matrix is given by

$$
\begin{aligned}
n_2(\boldsymbol{x},\boldsymbol{x}'\,|\,\boldsymbol{y},\boldsymbol{y}') &\equiv \langle\,\Psi\,|\,\psi^\dagger(\boldsymbol{y}')\,\psi^\dagger(\boldsymbol{y})\,\psi(\boldsymbol{x})\,\psi(\boldsymbol{x}')\,|\,\Psi\,\rangle \\
&= N(N-1)\int d^dx_3\cdots\int d^dx_N\,\Psi^*(\boldsymbol{y},\boldsymbol{y}',\boldsymbol{x}_3,\ldots,\boldsymbol{x}_N)\,\Psi(\boldsymbol{x},\boldsymbol{x}',\boldsymbol{x}_3,\ldots,\boldsymbol{x}_N)\quad.
\end{aligned}
\tag{8.29}
$$

Note the sum rules upon integrating the diagonal elements, *viz.*

$$
\int d^dx\,n_1(\boldsymbol{x}\,|\,\boldsymbol{x}) = N
$$
$$
\int d^dx\int d^dx'\,n_2(\boldsymbol{x},\boldsymbol{x}'\,|\,\boldsymbol{x},\boldsymbol{x}') = N(N-1)\quad.
\tag{8.30}
$$

In a plane wave basis, we write

$$
\psi_{\boldsymbol{k}} = \frac{1}{\sqrt{V}}\int d^dx\,\psi(\boldsymbol{x})\,e^{-i\boldsymbol{k}\cdot\boldsymbol{x}}
\tag{8.31}
$$

and therefore

$$
\begin{aligned}
\langle\,\Psi\,|\,\psi_{\boldsymbol{k}}^\dagger\psi_{\boldsymbol{k}'}\,|\,\Psi\,\rangle &= \frac{1}{V}\int d^dx\int d^dr\,e^{i(\boldsymbol{k}-\boldsymbol{k}')\cdot\boldsymbol{x}}\,e^{-i\boldsymbol{k}'\cdot\boldsymbol{r}}\,\langle\,\Psi\,|\,\psi^\dagger(\boldsymbol{x})\,\psi(\boldsymbol{x}+\boldsymbol{r})\,|\,\Psi\,\rangle \\
&= \delta_{\boldsymbol{k},\boldsymbol{k}'}\int d^dr\,e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\,\langle\,\Psi\,|\,\psi^\dagger(\boldsymbol{0})\,\psi(\boldsymbol{r})\,|\,\Psi\,\rangle \\
&= \delta_{\boldsymbol{k},\boldsymbol{k}'}\int d^dr\,e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\int d^dx_2\cdots\int d^dx_N\,\Psi^*(\boldsymbol{0},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)\,\Psi(\boldsymbol{r},\boldsymbol{x}_2,\ldots,\boldsymbol{x}_N)\quad.
\end{aligned}
\tag{8.32}
$$

### 8.1.2  The second quantized Hamiltonian

Now consider the action of permutation-symmetric first quantized operators such as the kinetic energy $\hat{T} = -\frac{\hbar^2}{2m}\sum_{i=1}^N\boldsymbol{\nabla}_i^2 = \sum_{i=1}^N\hat{t}_i$ and the potential energy $\hat{U} = \sum_{i<j}^N u(\boldsymbol{x}_i-\boldsymbol{x}_j)$. For a one-body operator such as $\hat{T}$, we have

$$
\begin{aligned}
\langle\,\alpha_1\cdots\alpha_N\,|\,\hat{T}\,|\,\alpha'_1\cdots\alpha'_N\,\rangle &= \int d^dx_1\cdots\int d^dx_N\left(\prod_\alpha n_\alpha!\right)^{-1/2}\left(\prod_\alpha n'_\alpha!\right)^{-1/2} \\
&\quad\times\sum_{\pi\in\mathcal{S}_N}(\pm1)^\pi\varphi^*_{\alpha_{\pi(1)}}(\boldsymbol{x}_1)\cdots\varphi^*_{\alpha_{\pi(N)}}(\boldsymbol{x}_N)\sum_{k=1}^N\hat{t}_i\,\varphi_{\alpha'_{\pi(1)}}(\boldsymbol{x}_1)\cdots\varphi_{\alpha'_{\pi(N)}}(\boldsymbol{x}_N) \\
&= \sum_{\pi\in\mathcal{S}_N}(\pm1)^\pi\left(\prod_\alpha n_\alpha!\,n'_\alpha!\right)^{-1/2}\sum_{i=1}^N\prod_{\substack{j\\(j\neq i)}}\delta_{\alpha_j,\alpha'_{\pi(j)}}\int d^dx_1\,\varphi^*_{\alpha_i}(\boldsymbol{x}_1)\,\hat{t}_1\,\varphi_{\alpha'_{\pi(i)}}(\boldsymbol{x}_1)\quad.
\end{aligned}
\tag{8.33}
$$

One may verify that any permutation-symmetric one-body operator such as $\hat{T}$ is faithfully represented by the second quantized expression,

$$\hat{T} = \sum_{\alpha,\beta} \langle \alpha \, | \, \hat{t} \, | \, \beta \rangle \, \psi_\alpha^\dagger \, \psi_\beta \quad , \tag{8.34}$$

where $\psi_\alpha^\dagger$ is $b_\alpha^\dagger$ or $c_\alpha^\dagger$ as the application determines, and

$$\langle \alpha \, | \, \hat{t} \, | \, \beta \rangle = \int d^d x \, \varphi_\alpha^*(\boldsymbol{x}) \, \hat{t}(\boldsymbol{\nabla}) \, \varphi_\beta(\boldsymbol{x}) \equiv \tau_{\alpha\beta} \quad . \tag{8.35}$$

Similarly,

$$\hat{V} = \sum_{\alpha,\beta} \langle \alpha \, | \, \hat{v}_{\text{ext}} \, | \, \beta \rangle \, \psi_\alpha^\dagger \, \psi_\beta \quad , \tag{8.36}$$

where

$$\langle \alpha \, | \, \hat{v}_{\text{ext}} \, | \, \beta \rangle = \int d^d x \, \varphi_\alpha^*(\boldsymbol{x}) \, \hat{v}_{\text{ext}}(\boldsymbol{x}) \, \varphi_\beta(\boldsymbol{x}) \equiv v_{\alpha\beta}^{\text{ext}} \quad . \tag{8.37}$$

Two-body operators such as $\hat{U}$ are represented as

$$\hat{U} = \tfrac{1}{2} \sum_{\alpha,\beta,\gamma,\delta} \langle \alpha\beta \, | \, \hat{u} \, | \, \gamma\delta \rangle \, \psi_\alpha^\dagger \, \psi_\beta^\dagger \, \psi_\delta \, \psi_\gamma \quad , \tag{8.38}$$

where

$$\langle \alpha\beta \, | \, \hat{u} \, | \, \gamma\delta \rangle = \int d^d x \int d^d x' \, \varphi_\alpha^*(\boldsymbol{x}) \, \varphi_\beta^*(\boldsymbol{x}') \, \hat{u}(\boldsymbol{x}, \boldsymbol{x}') \, \varphi_\delta(\boldsymbol{x}') \, \varphi_\gamma(\boldsymbol{x}) \equiv u_{\alpha\beta\gamma\delta} \quad . \tag{8.39}$$

The general form for an $n$-body operator is then

$$\hat{R} = \frac{1}{n!} \sum_{\substack{\alpha_1 \cdots \alpha_n \\ \beta_1 \cdots \beta_n}} \langle \alpha_1 \cdots \alpha_n \, | \, \hat{r} \, | \, \beta_1 \cdots \beta_n \rangle \, \psi_{\alpha_n}^\dagger \cdots \psi_{\alpha_n}^\dagger \, \psi_{\beta_n} \cdots \psi_{\beta_1} \tag{8.40}$$

where

$$\langle \alpha_1 \cdots \alpha_n \, | \, \hat{r} \, | \, \beta_1 \cdots \beta_n \rangle = \int d^d x_1 \cdots \int d^d x_n \, \varphi_{\alpha_1}^*(\boldsymbol{x}_1) \cdots \varphi_{\alpha_n}^*(\boldsymbol{x}_n) \, \hat{r}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n) \, \varphi_{\beta_n}(\boldsymbol{x}_n) \cdots \varphi_{\beta_1}(\boldsymbol{x}_1) \quad . \tag{8.41}$$

If the particles have no internal degrees of freedom, then the operators $\hat{r}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n)$ are just functions of the spatial coordinates $\{\boldsymbol{x}_i\}$. If there are (discrete) internal degrees of freedom, then $\hat{r}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_n)$ also has operator content in the internal Hilbert space as well.

Finally, if the Hamiltonian is noninteracting, consisting solely of one-body operators, then

$$\hat{H} = \sum_\alpha \varepsilon_\alpha \, \psi_\alpha^\dagger \, \psi_\alpha \quad , \tag{8.42}$$

where $\{\varepsilon_\alpha\}$ is the spectrum of the single particle Hamiltonian.

## 8.2 Hartree-Fock Theory

Consider the interacting electron Hamiltonian

$$\hat{H} = \sum_{i=1}^{N} \left\{ -\frac{\hbar^2}{2m} \boldsymbol{\nabla}_i^2 + v(\boldsymbol{x}_i) \right\} + \sum_{i<j}^{N} u(\boldsymbol{x}_i - \boldsymbol{x}_j) \quad . \tag{8.43}$$

We now endeavor to construct the best possible single Slater determinant state,

$$\Psi(\boldsymbol{x}_1 \, \sigma_1 \, , \, \ldots \, , \, \boldsymbol{x}_N \, \sigma_N) = \frac{1}{\sqrt{N!}} \, \mathcal{A} \left[ \varphi_{\alpha_1}(\boldsymbol{x}_1, \sigma_1) \cdots \varphi_{\alpha_N}(\boldsymbol{x}_N, \sigma_N) \right]$$

$$= \frac{1}{\sqrt{N!}} \sum_{\pi \in \mathcal{S}_N} \mathsf{sgn}(\pi) \prod_{i=1}^{N} \varphi_{\alpha_i}(\boldsymbol{x}_{\pi(i)} \, , \, \sigma_{\pi(i)}) \quad , \tag{8.44}$$

where $\mathcal{A}$ is the antisymmetrizer, and $\varphi_\alpha(\boldsymbol{x}, \sigma)$ is a single particle wavefunction. Typically we will take $\alpha = (j, \gamma)$ to be a composite label, and write

$$\varphi_\alpha(\boldsymbol{x}, \sigma) = \varphi_j(\boldsymbol{x}) \, \eta_\gamma(\sigma) \quad , \tag{8.45}$$

with $\eta_\gamma(\sigma) = \delta_{\sigma\gamma}$. In second-quantized notation, the wavefunction is given by

$$| \, \Psi \, \rangle = \prod_{\alpha}^{\mathsf{OCC}} c_\alpha^\dagger \, | \, 0 \, \rangle \quad . \tag{8.46}$$

The set OCC comprises the $N$ distinct *occupied* orbitals.

The second-quantized Hamiltonian is

$$\hat{H} = \int d^d x \, \psi_\sigma^\dagger(\boldsymbol{x}) \left\{ -\frac{\hbar^2}{2m} \delta_{\sigma\tau} \boldsymbol{\nabla}^2 + v_{\sigma\tau}^{\mathsf{ext}}(\boldsymbol{x}) \right\} \psi_\tau(\boldsymbol{x})$$

$$+ \tfrac{1}{2} \int d^d x \int d^d x' \, \psi_\sigma^\dagger(\boldsymbol{x}) \, \psi_{\sigma'}^\dagger(\boldsymbol{x}') \, u_{\sigma\tau\sigma'\tau'}(\boldsymbol{x} - \boldsymbol{x}') \, \psi_{\tau'}(\boldsymbol{x}') \, \psi_\tau(\boldsymbol{x}) \quad , \tag{8.47}$$

where $\{\sigma, \tau, \sigma', \tau'\}$ are spin polarizations, and where the two-body interaction for spin-isotropic systems is written as

$$u_{\sigma\tau\sigma'\tau'}(\boldsymbol{x} - \boldsymbol{x}') = u^{\mathsf{SCALAR}}(\boldsymbol{x} - \boldsymbol{x}') \, \delta_{\sigma\tau} \, \delta_{\sigma'\tau'} + u^{\mathsf{SPIN}}(\boldsymbol{x} - \boldsymbol{x}') \, \boldsymbol{\sigma}_{\sigma\tau} \cdot \boldsymbol{\sigma}_{\sigma'\tau'} \quad . \tag{8.48}$$

Here $u^{\mathsf{SCALAR}}$ is the scalar component and $u^{\mathsf{SPIN}}$ the Heisenberg component of the two-body interaction, and $\boldsymbol{\sigma}$ are the Pauli matrices. Throughout we adopt the Einstein convention over summing over repeated indices.

In order to evaluate the expectation value $E = \langle \Psi \,|\, \hat{H} \,|\, \Psi \rangle$, we need the following:

$$\langle\Psi|\psi_\sigma^\dagger(\boldsymbol{x})\psi_\tau(\boldsymbol{y})|\Psi\rangle = \sum_\alpha^{\text{occ}} \varphi_\alpha^*(\boldsymbol{x},\sigma)\,\varphi_\alpha(\boldsymbol{y},\tau) \tag{8.49}$$

$$\langle\Psi|\psi_\sigma^\dagger(\boldsymbol{x})\psi_{\sigma'}^\dagger(\boldsymbol{x}')\psi_{\tau'}(\boldsymbol{x}')\psi_\tau(\boldsymbol{x})|\Psi\rangle = \sum_{\alpha,\beta}^{\text{occ}} \varphi_\alpha^*(\boldsymbol{x},\sigma)\,\varphi_\beta^*(\boldsymbol{x}',\sigma')\Big(\varphi_\alpha(\boldsymbol{x},\tau)\varphi_\beta(\boldsymbol{x}',\tau') - \varphi_\beta(\boldsymbol{x},\tau)\,\varphi_\alpha(\boldsymbol{x}',\tau')\Big) \quad .$$

This generalizes to

$$\langle \Psi \,|\, \psi_{\sigma_1}^\dagger(\boldsymbol{x}_1)\cdots\psi_{\sigma_n}^\dagger(\boldsymbol{x}_n)\,\psi_{\tau_n}(\boldsymbol{x}_n)\cdots\psi_{\tau_1}(\boldsymbol{x}_1) \,|\, \Psi \rangle = \sum_{\alpha_1\cdots\alpha_n}^{\text{occ}} \left(\prod_{i=1}^n \varphi_{\alpha_i}^*(\boldsymbol{x}_i,\sigma_i)\right) \det\big[\varphi_{\alpha_j}(\boldsymbol{x}_k,\tau_k)\big] \quad .$$
$$\tag{8.50}$$

The RHS is necessarily zero if $n > N$ because there is then a linear dependence among the rows of the matrix $M_{j,k} = \det\big[\varphi_{\alpha_j}(\boldsymbol{x}_k,\sigma_k)\big]$.

We now have $E = T + V + U$, with

$$T = \sum_\alpha^{\text{occ}} \int d^dx\, \varphi_\alpha^*(\boldsymbol{x},\sigma)\,\hat{t}_{\sigma\tau}(\boldsymbol{\nabla})\,\varphi_\alpha(\boldsymbol{x},\tau) \qquad , \qquad V = \sum_\alpha^{\text{occ}} \int d^dx\, \varphi_\alpha^*(\boldsymbol{x},\sigma)\,\hat{v}_{\sigma\tau}^{\text{ext}}(\boldsymbol{x})\,\varphi_\alpha(\boldsymbol{x},\tau) \tag{8.51}$$

and

$$U = \tfrac{1}{2}\sum_{\alpha,\beta}^{\text{occ}} \int d^dx \int d^dx'\, u_{\sigma\tau\sigma'\tau'}(\boldsymbol{x}-\boldsymbol{x}')\,\varphi_\alpha^*(\boldsymbol{x},\sigma)\,\varphi_\beta^*(\boldsymbol{x}',\sigma')\Big(\varphi_\alpha(\boldsymbol{x},\tau)\,\varphi_\beta(\boldsymbol{x}',\tau') - \varphi_\beta(\boldsymbol{x},\tau)\,\varphi_\alpha(\boldsymbol{x}',\tau')\Big) \quad .$$

Now let's functionally vary with respect to the wavefunction $\varphi_\alpha^*(\boldsymbol{x},\sigma)$. We have

$$\frac{\delta T}{\delta\varphi_\alpha^*(\boldsymbol{x},\sigma)} = \hat{t}_{\sigma\tau}(\boldsymbol{\nabla})\,\varphi_\alpha(\boldsymbol{x},\tau) \qquad , \qquad \frac{\delta V}{\delta\varphi_\alpha^*(\boldsymbol{x},\sigma)} = \hat{v}_{\sigma\tau}^{\text{ext}}(\boldsymbol{x})\,\varphi_\alpha(\boldsymbol{x},\tau) \tag{8.52}$$

and

$$\frac{\delta U}{\delta\varphi_\alpha^*(\boldsymbol{x},\sigma)} = \int d^dx'\, u_{\sigma\tau\sigma'\tau'}(\boldsymbol{x}-\boldsymbol{x}') \sum_\beta^{\text{occ}} \varphi_\beta^*(\boldsymbol{x}',\sigma')\Big(\varphi_\alpha(\boldsymbol{x},\tau)\,\varphi_\beta(\boldsymbol{x}',\tau') - \varphi_\beta(\boldsymbol{x},\tau)\,\varphi_\alpha(\boldsymbol{x}',\tau')\Big) \quad .$$
$$\tag{8.53}$$

In order to maintain orthonormality of the single particle wavefunctions, *i.e.* $\langle\varphi_\alpha\,|\,\varphi_\beta\rangle = \delta_{\alpha\beta}$, we extremize not $E$ but rather $E^*$, where

$$E^* = T + V + U - \sum_{\alpha,\beta} \Lambda_{\alpha\beta}\Big(\langle\varphi_\alpha\,|\,\varphi_\beta\rangle - \delta_{\alpha\beta}\Big) \quad , \tag{8.54}$$

where the $\{\Lambda_{\alpha\beta}\}$ are a set of Lagrange multipliers. The condition $\delta E^* = 0$ now yields

$$
\left\{ -\frac{\hbar^2}{2m} \delta_{\sigma\tau} \boldsymbol{\nabla}^2 + v_{\sigma\tau}^{\text{ext}}(\boldsymbol{x}) + \int d^d x'\, u_{\sigma\tau\sigma'\tau'}(\boldsymbol{x} - \boldsymbol{x}') \sum_{\beta}^{\text{occ}} \varphi_{\beta}^*(\boldsymbol{x}', \sigma')\, \varphi_{\beta}(\boldsymbol{x}', \tau') \right\} \varphi_{\alpha}(\boldsymbol{x}, \tau)
$$
$$
- \int d^d x'\, u_{\sigma\tau\sigma'\tau'}(\boldsymbol{x} - \boldsymbol{x}')\, \varphi_{\alpha}(\boldsymbol{x}', \tau') \sum_{\beta}^{\text{occ}} \varphi_{\beta}^*(\boldsymbol{x}', \sigma')\, \varphi_{\beta}(\boldsymbol{x}, \tau) = \sum_{\beta}^{\text{occ}} \Lambda_{\alpha\beta}\, \varphi_{\beta}(\boldsymbol{x}, \sigma) \quad . \tag{8.55}
$$

One can show that the matrix $\Lambda$ must be Hermitian, which means it can be diagonalized by a unitary matrix $U_{a\alpha}$, with $(U \Lambda U^{\dagger})_{ab} = \varepsilon_a\, \delta_{ab}$. Defining $\varphi_a(\boldsymbol{x}, \sigma) = U_{a\alpha}\, \varphi_{\alpha}(\boldsymbol{x}, \sigma)$, we then obtain the *Hartree-Fock equations*,

$$
\left\{ -\frac{\hbar^2}{2m} \delta_{\sigma\tau} \boldsymbol{\nabla}^2 + v_{\sigma\tau}^{\text{ext}}(\boldsymbol{x}) + \int d^d x'\, u_{\sigma\tau\sigma'\tau'}(\boldsymbol{x} - \boldsymbol{x}') \sum_{b}^{\text{occ}} \varphi_{b}^*(\boldsymbol{x}', \sigma')\, \varphi_{b}(\boldsymbol{x}', \tau') \right\} \varphi_{a}(\boldsymbol{x}, \tau)
$$
$$
- \int d^d x'\, u_{\sigma\tau\sigma'\tau'}(\boldsymbol{x} - \boldsymbol{x}')\, \varphi_{a}(\boldsymbol{x}', \tau') \sum_{b}^{\text{occ}} \varphi_{b}^*(\boldsymbol{x}', \sigma')\, \varphi_{b}(\boldsymbol{x}, \tau) = \varepsilon_a\, \varphi_{a}(\boldsymbol{x}, \sigma) \quad , \tag{8.56}
$$

with no sum on $a$. The quantities $\{\varepsilon_a\}$ are the *single particle Hartree-Fock energies*. Note that the last term in the curly brackets can be interpreted as a renormalization of the one-body potential, with

$$
v_{\sigma\tau}^{\text{H}}(\boldsymbol{x}) = \int d^d x'\, u_{\sigma\tau\sigma'\tau'}(\boldsymbol{x} - \boldsymbol{x}') \sum_{b}^{\text{occ}} \varphi_{b}^*(\boldsymbol{x}', \sigma')\, \varphi_{b}(\boldsymbol{x}', \tau') \quad . \tag{8.57}
$$

This is known as the *Hartree potential*. The *Fock term*, arising from exchange, has the interpretation of a *nonlocal* potential, *viz.*

$$
v_{\sigma\tau}^{\text{F}}(\boldsymbol{x}, \boldsymbol{x}') = -u_{\sigma\tau'\sigma'\tau}(\boldsymbol{x} - \boldsymbol{x}') \sum_{b}^{\text{occ}} \varphi_{b}^*(\boldsymbol{x}', \sigma')\, \varphi_{b}(\boldsymbol{x}, \tau') \quad . \tag{8.58}
$$

Thus, the Hartree-Fock (HF) equations may be written

$$
\left\{ -\frac{\hbar^2}{2m} \delta_{\sigma\tau} \boldsymbol{\nabla}^2 + v_{\sigma\tau}^{\text{ext}}(\boldsymbol{x}) + v_{\sigma\tau}^{\text{H}}(\boldsymbol{x}) \right\} \varphi_{a}(\boldsymbol{x}, \tau) + \int d^d x'\, v_{\sigma\tau}^{\text{F}}(\boldsymbol{x}, \boldsymbol{x}')\, \varphi_{a}(\boldsymbol{x}', \tau) = \varepsilon_a\, \varphi_{a}(\boldsymbol{x}, \sigma) \quad . \tag{8.59}
$$

Note that if we multiply Eqn. 8.56 by $\varphi_a^*(\boldsymbol{x}, \sigma)$ and then integrate over $\boldsymbol{x}$ and sum on $\sigma$, we obtain the relation

$$
\varepsilon_a = \int d^d x\, \varphi_a^*(\boldsymbol{x}, \sigma) \left\{ -\frac{\hbar^2}{2m} \delta_{\sigma\tau} \boldsymbol{\nabla}^2 + v_{\sigma\tau}^{\text{ext}}(\boldsymbol{x}) + v_{\sigma\tau}^{\text{H}}(\boldsymbol{x}) \right\} \varphi_{\alpha}(\boldsymbol{x}, \tau)
$$
$$
+ \int d^d x \int d^d x'\, v_{\sigma\tau}^{\text{F}}(\boldsymbol{x}, \boldsymbol{x}')\, \varphi_a^*(\boldsymbol{x}, \sigma)\, \varphi_a(\boldsymbol{x}', \tau) \quad . \tag{8.60}
$$

If we now sum over all occupied states $a$, we obtain the result

$$\sum_a^{\text{occ}} \varepsilon_a = T + V + 2U \quad . \tag{8.61}$$

Thus, the sum over all the single particle HF energies *is not* the total energy $E = \langle \Psi \,|\, \hat{H} \,|\, \Psi \rangle$. Rather, the interpretation of $\varepsilon_a$ is that

$$\frac{\delta E}{\delta N} = E(N) - E(N-1) = \varepsilon_a \tag{8.62}$$

when the electron in state $a$ is removed to form the $(N-1)$-electron system. Put another way, the energy required to transfer an electron from an orbital $|\,a\,\rangle$ to an orbital $|\,b\,\rangle$ is $\varepsilon_b - \varepsilon_a$. These results presume that this transfer does not affect the other wavefunctions $\varphi_c(\boldsymbol{x},\sigma)$ for $c \neq a, b$. This is presumably valid in the thermodynamic limit $N \to \infty$, but need not be so for finite $N$. The difference in ground state energies is thus given by the smallest value $\min_a \varepsilon_a$.

When $v_{\sigma\tau}^{\text{ext}}(\boldsymbol{x}) = v(\boldsymbol{x})\,\delta_{\sigma\tau}$ and $u_{\sigma\tau\sigma'\tau'}(\boldsymbol{x} - \boldsymbol{x}') = u(\boldsymbol{x} - \boldsymbol{x}')\,\delta_{\sigma\tau}\,\delta_{\sigma'\tau'}$, the spin degree of freedom is just a spectator, and we may obtain a solution where the states are labeled by an index $j \in \{1,\ldots,N\}$ and a spin polarization $\sigma \in \{\uparrow,\downarrow\}$, with polarization-independent single particle HF energies $\varepsilon_j$. The HF equations then become

$$\left\{ -\frac{\hbar^2}{2m}\,\boldsymbol{\nabla}^2 + v_{\text{ext}}(\boldsymbol{x}) + v^{\text{H}}(\boldsymbol{x}) \right\} \varphi_j(\boldsymbol{x}) + \int d^dx'\, v^{\text{F}}(\boldsymbol{x} - \boldsymbol{x})\, \varphi_j(\boldsymbol{x}') = \varepsilon_j\, \varphi_j(\boldsymbol{x}) \quad , \tag{8.63}$$

where

$$v^{\text{H}}(\boldsymbol{x}) = 2 \int d^dx'\, u(\boldsymbol{x} - \boldsymbol{x}') \sum_l^{\text{occ}} |\varphi_l(\boldsymbol{x}')|^2$$

$$v^{\text{F}}(\boldsymbol{x}, \boldsymbol{x}') = -u(\boldsymbol{x} - \boldsymbol{x}') \sum_l^{\text{occ}} \varphi_l^*(\boldsymbol{x}')\, \varphi_l(\boldsymbol{x}) \quad . \tag{8.64}$$

**Translationally invariant systems**

For translationally invariant systems, the plane wave basis $\varphi_{\boldsymbol{k}}(\boldsymbol{x}) = V^{-1/2} \exp(i\boldsymbol{k} \cdot \boldsymbol{x})$ yields a solution. The Hartree and Fock potentials are then

$$v^{\text{H}}(\boldsymbol{x}) = n\,\hat{u}(0)$$

$$v_{\text{F}}(\boldsymbol{x} - \boldsymbol{x}') = -u(\boldsymbol{x} - \boldsymbol{x}') \int \frac{d^dk}{(2\pi)^d}\, e^{i\boldsymbol{k} \cdot (\boldsymbol{x} - \boldsymbol{x}')}\, \Theta(k_{\text{F}} - k) \quad , \tag{8.65}$$

where

$$n = 2 \int \frac{d^dk}{(2\pi)^d}\, \Theta(k_{\text{F}} - k) = \frac{2\Omega_d\, k_{\text{F}}^d}{d\,(2\pi)^d} \tag{8.66}$$

is the number density. Here $\Omega_d = 2\pi^{d/2}/\Gamma(d/2)$ is the total solid angle in $d$ space dimensions. One then has the Hartree-Fock energies

$$\varepsilon(\boldsymbol{k}) = \frac{\hbar^2 \boldsymbol{k}^2}{2m} + n\,\hat{u}(0) - \int \frac{d^d k'}{(2\pi)^d}\,\hat{u}(\boldsymbol{k} - \boldsymbol{k}')\,\Theta(k_{\mathrm{F}} - k') \quad, \tag{8.67}$$

where $\hat{u}(\boldsymbol{k})$ is the Fourier transform of $u(\boldsymbol{x})$.

**HF theory for atoms**

In atomic physics, we have the one-body ion core potential $v^{\mathrm{ext}}(\boldsymbol{x}) = -Ze^2/|\boldsymbol{x}|$ (neglecting spin-orbit effects) and the two-body electron-electron interaction $u(\boldsymbol{x} - \boldsymbol{x}') = e^2/|\boldsymbol{x} - \boldsymbol{x}'|$. It is then a good approximation to assume that the Hartree-Fock wavefunctions $\varphi_i(\boldsymbol{x})$ are of the form

$$\varphi_\alpha(\boldsymbol{x}) = R_{nl}(r)\,Y_{lm}(\theta, \phi) \quad, \tag{8.68}$$

independent of $\sigma$. This follows from the rotational isotropy of the ion core potential. We can then classify the single particle states by the quantum numbers $n \in \{1, 2, \ldots\}$, $l \in \{0, 1, \ldots, n-1\}$, $m_l \in \{-l, \ldots, +l\}$, and $m_s = \pm\frac{1}{2}$. The essential physics introduced by the Hartree-Fock method is that of *screening*. Close to the origin, a given electron senses a potential $-Ze^2/r$ due to the unscreened nucleus. Farther away, though, the nuclear charge is screened by the core electrons, and the potential decays faster than $1/r$.[2] Whereas states of different $l$ and identical $n$ are degenerate for the noninteracting hydrogenic atom, when the nuclear potential is screened, states of different $l$ are no longer degenerate. Smaller $l$ means lower energy, since these states are localized closer to the nucleus, where the potential is large and negative and relatively unscreened. Based on the HF energy levels, the order in which the electron shells are filled throughout the periodic table is roughly given by that in Fig. 8.1. This is known as the *Aufbau principle* from the German *Aufbau* = "building up" (see Fig. 8.1). The order in which the orbitals are filled follows the *diagonal rule*, which says that orbitals with lower values of $n + l$ are filled before those with higher values, and that in the case of equal $n + l$ values, the orbital with the lower $n$ is filled first. For a given $l$ and $n$ there are $(2s + 1) \times (2l + 1) = 4l + 2$ states ($s = \frac{1}{2}$), labeled by the angular momentum and spin polarization quantum numbers $m_l$ and $m_s$; this group of orbitals is called a *shell*.

**HF theory for the electron gas**

The so-called *jellium* model of the electron gas consists of $N$ electrons moving in a uniform neutralizing (*i.e.* positively charged) background. The system is translationally invariant, hence the HF wavefunctions are labeled by wavevectors $\boldsymbol{k}$, with $\varphi_{\boldsymbol{k}}(\boldsymbol{x}) = V^{-1/2}\exp(i\boldsymbol{k} \cdot \boldsymbol{x})$. In all

---

[2]Within the Thomas-Fermi approximation, the potential at long distances decays as $-\mathcal{C}e^2 a_{\mathrm{B}}^3/r^4$, where $\mathcal{C} \simeq 100$ is a numerical factor, independent of $Z$.
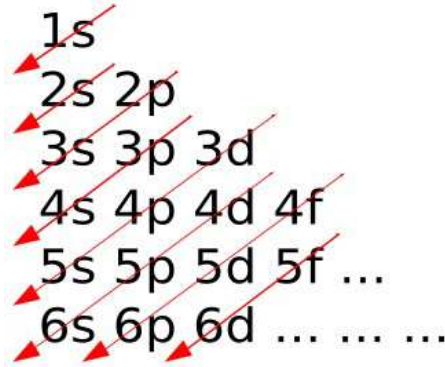
Figure 8.1: The *Aufbau* principle and the diagonal rule. Image credit: Wikipedia.

dimensions, the neutralizing background contributions precisely cancel the Hartree term in the energy. The single particle HF energies are then given by ($d = 3$ dimensions assumed)

$$\varepsilon(\boldsymbol{k}) = \frac{\hbar^2 \boldsymbol{k}^2}{2m} - \int \frac{d^3 k'}{(2\pi)^3} \frac{4\pi e^2}{(\boldsymbol{k} - \boldsymbol{k}')^2} \, \Theta(k_{\mathrm{F}} - k') = \varepsilon_0(\boldsymbol{k}) + \Sigma(\boldsymbol{k}) \quad , \tag{8.69}$$

where $n = k_{\mathrm{F}}^3 / 3\pi^2$ is the electron density. The *bare dispersion* for noninteracting electrons is $\varepsilon_0(\boldsymbol{k}) = \hbar^2 \boldsymbol{k}^2 / 2m$, and the *self-energy* is

$$\Sigma(\boldsymbol{k}) = \frac{e^2 k_{\mathrm{F}}}{2\pi} \left( \frac{k^2 - k_{\mathrm{F}}^2}{k k_{\mathrm{F}}} \ln \left| \frac{k + k_{\mathrm{F}}}{k - k_{\mathrm{F}}} \right| - 2 \right) \quad . \tag{8.70}$$

If we expand about the Fermi wavevector, writing $\boldsymbol{k} = (k_{\mathrm{F}} + q) \, \hat{\boldsymbol{n}}$, where $\hat{\boldsymbol{n}}$ is any unit vector, we obtain

$$\varepsilon(k_{\mathrm{F}} + q) = \varepsilon_{\mathrm{F}} + \frac{\hbar^2 k_{\mathrm{F}}}{m} q + \frac{e^2}{\pi} q \ln \left| \frac{2k_{\mathrm{F}}}{q} \right| + \mathcal{O}(q^2) \quad , \tag{8.71}$$

where $\varepsilon_{\mathrm{F}} = \frac{\hbar^2 k_{\mathrm{F}}^2}{2m} - \frac{e^2 k_{\mathrm{F}}}{\pi}$ is the Fermi energy within HF theory. The velocity in the vicinity perpendicular to the Fermi surface is then with

$$v(q) = \frac{1}{\hbar} \frac{\partial \varepsilon(k_{\mathrm{F}} + q)}{\partial q} = \frac{\hbar k_{\mathrm{F}}}{m} + \frac{e^2}{\pi \hbar} \left( \ln \left| \frac{2k_{\mathrm{F}}}{q} \right| - 1 \right) \quad , \tag{8.72}$$

which diverges logarithmically in the limit $q \to 0$. This divergence of the Fermi velocity is an artifact of the HF approach, which neglects screening effects, which we shall consider later on.

The total kinetic energy per particle is given by

$$\frac{T}{N} = \frac{1}{N} \times 2 \sum_{|\boldsymbol{k}| < k_{\mathrm{F}}} \varepsilon_0(k) = \frac{2}{n} \int \frac{d^3 k}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} \Theta(k_{\mathrm{F}} - k) = \frac{3\hbar^2 k_{\mathrm{F}}^2}{10m} \quad . \tag{8.73}$$

The total potential energy comes from the sum of the (i) self-interaction of the neutralizing background, (ii) the energy of interaction between the neutralizing background and the uniform density electron gas, (iii) the Hartree energy of the electron gas $E_H$, and (iv) the exchange energy of the electron gas $E_X$. The first three of these sum to zero, leaving $E_X$, where

$$
\begin{aligned}
\frac{E_X}{N} &= \frac{1}{2N} \times 2 \sum_{|\boldsymbol{k}| < k_F} \Sigma(k) = \frac{1}{n} \int \frac{d^3k}{(2\pi)^3} \, \Sigma(k) \, \Theta(k_{\scriptscriptstyle F} - k) \\
&= -\frac{e^2 k_F}{4\pi^3} \int_0^1 dx \, x^2 \left\{ 2 + \frac{1 - x^2}{x} \, \ln \left| \frac{1+x}{1-x} \right| \right\} = -\frac{3e^2 k_F}{4\pi}
\end{aligned}
$$

(8.74)

Note the factor of $\frac{1}{2}$ multiplying the above result, which corrects for the factor of 2 in Eqn. 8.61.

It is conventional to define a dimensionless length $r_s$ according to $\frac{4}{3}\pi(r_s\, a_B)^3\, n \equiv 1$, where $a_B = \hbar^2/me^2$ is the Bohr radius. Thus

$$
r_s = \left( \frac{3}{4\pi} \right)^{1/3} n^{-1/3} a_B^{-1} \quad , \quad k_{\scriptscriptstyle F} = \left( \frac{9\pi}{4} \right)^{1/3} r_s^{-1} a_B^{-1} \quad .
$$

(8.75)

The kinetic energy per particle is then

$$
\frac{T}{N} = \frac{3\hbar^2}{10m} \left( \frac{9\pi}{4} \right)^{2/3} r_s^{-2} a_B^{-2} = \frac{3}{5} \left( \frac{9\pi}{4} \right)^{2/3} \frac{e^2}{2a_B} \cdot \frac{1}{r_s^2} \simeq \frac{2.21}{r_s^2} \, \mathrm{Ryd} \quad ,
$$

(8.76)

while the exchange energy per particle is

$$
\frac{E_X}{N} = -\frac{3}{2\pi} \left( \frac{9\pi}{4} \right)^{1/3} \frac{e^2}{2a_B} \cdot \frac{1}{r_s} \simeq -\frac{0.916}{r_s} \, \mathrm{Ryd} \quad ,
$$

(8.77)

where $1\,\mathrm{Ryd} = e^2/2a_B = 13.6057\,\mathrm{eV}$. Thus, interaction effects dominate when $r_s$ is large, meaning the density $n$ is small. This is because the kinetic energy term involves two gradients, hence scales as $L^{-2}$, whereas the Coulomb interaction scales as $L^{-1}$. For short-ranged interactions, interaction effects dominate at large densities, which perhaps is more intuitive.

## 8.3 Density Functional Theory

In any interacting electronic system, the kinetic energy of each electron is given by $\boldsymbol{p}^2/2m$ and the interaction between any two electrons is the Coulomb energy $v(\boldsymbol{x} - \boldsymbol{x}') = e^2/|\boldsymbol{x} - \boldsymbol{x}'|$. What differs in the description from one material to the next is the one-body potential $v_{\mathrm{ext}}(\boldsymbol{x})$. This is what distinguishes the Hamiltonian for table salt (NaCl) from that of elemental iron (Fe)[3]. Thus,

---

[3]For large $Z$ ions, the spin-orbit interaction is also important. This can be included in the one-body potential $v_{\mathrm{ext}}(\boldsymbol{x})$ by extending $v_{\mathrm{ext}}$ to a function $v_{\mathrm{ext}}(\boldsymbol{x}, \boldsymbol{p}, \boldsymbol{\sigma})$ of position, momentum, and spin.

the ground state wavefunction of any many-electron system $\Psi_{\sigma_1 \cdots \sigma_N}(\boldsymbol{x}_1, \ldots \boldsymbol{x}_N)$ is completely determined by $v_{\text{ext}}(\boldsymbol{x})$. From the wavefunction we can also determine the one-body electron density for spin polarization $\sigma$, which is

$$
n_\sigma(\boldsymbol{x}) = \langle\, \Psi\, |\, \psi_\sigma^\dagger(\boldsymbol{x})\, \psi_\sigma(\boldsymbol{x})\, |\, \Psi\, \rangle = N \sum_{\sigma_2} \cdots \sum_{\sigma_N} \int d^3x_2 \cdots \int d^3x_N \, \big| \Psi_{\sigma\, \sigma_2 \cdots \sigma_N}(\boldsymbol{x}, \boldsymbol{x}_2, \ldots \boldsymbol{x}_N) \big|^2 \quad .
\tag{8.78}
$$

Summing over both spin polarizations, we obtain the total electron number density,

$$
n(\boldsymbol{x}) = \sum_\sigma n_\sigma(\boldsymbol{x}) \quad .
\tag{8.79}
$$

Though at first consideration counterintuitive, it turns out that the entire ground state wavefunction can be considered to be a *functional* of the electron number density. A number of highly consequential and extremely useful results follow. This is the subject of *density functional theory* (DFT), which revolutionized the study of electronic structure of molecules and solids[4], and which was recognized by the 1998 Nobel Prize in Chemistry to Walter Kohn and John Pople.

### 8.3.1　Hohenberg-Kohn theorems

The mathematical basis underpinning DFT are two theorems by Hohenberg and Kohn.

THEOREM #1 : The ground state energy of a many-electron system is a functional of the total electron density $n(\boldsymbol{x}) = \sum_\sigma \langle\, \Psi\, |\, \psi_\sigma^\dagger(\boldsymbol{x})\, \psi_\sigma(\boldsymbol{x})\, |\, \Psi\, \rangle$.

To prove this theorem – in our callow physicist's sort of way – let $|\,\Psi\,\rangle$ and $|\,\Psi'\,\rangle$ be the ground states corresponding respectively to the two external potentials $v_{\text{ext}}(\boldsymbol{x})$ and $v'_{\text{ext}}(\boldsymbol{x})$. We assume these ground states are normalized and distinct, meaning that in any finite volume their overlap is less than unity in magnitude. The Hamiltonians are $\hat{H} = \hat{T} + \hat{V} + \hat{U}$ and $\hat{H}' = \hat{T} + \hat{V}' + \hat{U}$, and it must be that

$$
E' = \langle\, \Psi'\, |\, H'\, |\, \Psi'\, \rangle < \langle\, \Psi\, |\, \hat{H}'\, |\, \Psi\, \rangle = \langle\, \Psi\, |\, \hat{H}\, |\, \Psi\, \rangle + \langle\, \Psi\, |\, \hat{V}' - \hat{V}\, |\, \Psi\, \rangle \quad ,
\tag{8.80}
$$

where

$$
\hat{V} = \int d^3x \, v_{\text{ext}}(\boldsymbol{x})\, \hat{n}(\boldsymbol{x}) \qquad , \qquad \hat{V}' = \int d^3x \, v'_{\text{ext}}(\boldsymbol{x})\, \hat{n}(\boldsymbol{x}) \quad .
\tag{8.81}
$$

Thus we conclude $E' < E + \langle\, \Psi\, |\, \hat{V}' - \hat{V}\, |\, \Psi\, \rangle$. But then $E < E' + \langle\, \Psi'\, |\, \hat{V} - \hat{V}'\, |\, \Psi'\, \rangle$ as well, simply by exchanging the definitions of the primed and unprimed systems. Adding these two results we obtain

$$
0 < \langle\, \Psi\, |\, \hat{V}' - \hat{V}\, |\, \Psi\, \rangle + \langle\, \Psi'\, |\, \hat{V} - \hat{V}'\, |\, \Psi'\, \rangle \quad .
\tag{8.82}
$$

---

[4]Here we follow the discussion in chapter 15 of Girvin and Yang, *Condensed Matter Physics* (Cambridge, 2019). See also G. Giuliani and G. Vignale, *Quantum Theory of the Electron Liquid* (Cambridge, 2005).

and thus if $\langle \Psi | \hat{n}(\boldsymbol{x}) | \Psi \rangle = \langle \Psi' | \hat{n}(\boldsymbol{x}) | \Psi' \rangle = n(\boldsymbol{x})$, we arrive at a contradiction: $0 < 0$. We conclude that the ground state wavefunctions for different one-body potentials cannot yield the exact same density $n(\boldsymbol{x})$.

THEOREM #2: The ground state energy may be expressed as a functional of the density, $E[n]$, such that minimizing this functional with respect to $n(\boldsymbol{x})$ yields the true ground state density.

To see that this is the case, note that theorem #1 entails that for each density $n(\boldsymbol{x})$ corresponding to the many-body ground state in some external potential, there is a corresponding ground state wavefunction $| \Psi[n] \rangle$. Now define the functional

$$
E[n] = \overbrace{\langle \Psi[n] | T + U | \Psi[n] \rangle}^{E_{\text{jel}}[n]} + \int d^3x \, v_{\text{ext}}(\boldsymbol{x}) \, n(\boldsymbol{x}) \quad . \tag{8.83}
$$

Here $E_{\text{jel}}[n]$ is the energy functional for jellium, with $v_{\text{ext}} = 0$. Note that this requires that we take the two-body potential term $\hat{U}$ to be

$$
\hat{U} = \frac{1}{2} \int d^3x \int d^3x' \, \big( \hat{n}(\boldsymbol{x}) - n_0 \big) \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} \big( \hat{n}(\boldsymbol{x}') - n_0 \big) \quad , \tag{8.84}
$$

where $n_0$ corresponds to a uniform neutralizing background. Charge neutrality requires that

$$
\lim_{N \to \infty} \frac{1}{N} \int d^3x \, \big( n(\boldsymbol{x}) - n_0 \big) = 0 \tag{8.85}
$$

lest the Coulomb energy diverge. Now, since $E[\tilde{n}] = \langle \Psi[\tilde{n}] | H | \Psi[\tilde{n}] \rangle > E[n]$, which follows by considering $| \Psi[\tilde{n}] \rangle$ to be a variational ground state for the Hamiltonian whose true ground state density is $n(\boldsymbol{x})$, we conclude that the functional $E[n]$ is indeed minimized when $n(\boldsymbol{x})$ is the true ground state density when the external potential is $v_{\text{ext}}(\boldsymbol{x})$.

How do we know that a given density $n(\boldsymbol{x})$ corresponds to the actual ground state density for Coulomb-interacting electrons in some external potential $v_{\text{ext}}(\boldsymbol{x})$? The short answer is that we don't. Indeed for the single particle system, where there are no Coulomb interactions, any density function $n(\boldsymbol{x})$ which vanishes at any location cannot possibly be the actual ground state density for any nonsingular potential $v_{\text{ext}}(\boldsymbol{x})$ due to the Perron-Frobenius "no nodes theorem". Functions $n(\boldsymbol{x})$ which do correspond to the ground state density of a fermionic system for some potential $v_{\text{ext}}(\boldsymbol{x})$ are called *V-representable*. A weaker condition is that of *N-representability*, which means that for a given density function $n(\boldsymbol{x})$, there exists an $N$-fermion wavefunction $\Psi_{\sigma_1 \cdots \sigma_N}(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$ such that

$$
\begin{aligned}
n(\boldsymbol{x}) &= \sum_\sigma \langle \Psi | \psi_\sigma^\dagger(\boldsymbol{x}) \, \psi_\sigma(\boldsymbol{x}) | \Psi \rangle \\
&= N \sum_\sigma \sum_{\sigma_2} \cdots \sum_{\sigma_N} \int d^3x_2 \cdots \int d^3x_N \, \big| \Psi_{\sigma \sigma_2 \cdots \sigma_N}(\boldsymbol{x}, \boldsymbol{x}_2, \ldots \boldsymbol{x}_N) \big|^2 \quad .
\end{aligned} \tag{8.86}
$$

Levy[5] and Lieb [6] showed that one could extend the domain of density functionals thusly, so that the energy minimization is to be carried out over all $|\Psi\rangle$ such that $\langle\Psi|\hat{n}(\boldsymbol{x})|\Psi\rangle = n(\boldsymbol{x})$, where $\hat{n}(\boldsymbol{x}) = \sum_\sigma \psi_\sigma^\dagger(\boldsymbol{x})\,\psi_\sigma(\boldsymbol{x})$. Note that while obtaining $n(\boldsymbol{x})$ from $|\Psi\rangle$ is formally defined by Eqn. 8.86, the inverse process, by which one extracts an $N$-body wavefunction $\Psi_{\sigma_1\cdots\sigma_N}(\boldsymbol{x}_1,\ldots,\boldsymbol{x}_N)$ from a given $N$-representable density function $n(\boldsymbol{x})$ is impractically complex for any $N > 1$. The virtue of the Kohn-Sham procedure, discussed in the next section, is that it provides us with a constructive way to implement the extremization procedure within a class of many-body wavefunctions.

### 8.3.2  Kohn-Sham equations

For Coulomb-interacting electrons, the functional $E_{\text{jel}}[n]$ is *universal* and is given by

$$E_{\text{jel}}[n] = \min_{|\Psi\rangle \to n(\boldsymbol{x})}\big\langle\,\Psi[n]\,|\,\hat{T}+\hat{U}\,|\,\Psi[n]\,\big\rangle \quad, \tag{8.87}$$

where the minimization is with respect to all totally antisymmetric $N$-body wavefunctions yielding a one-body density $n(\boldsymbol{x})$. For *noninteracting* systems, the ground state is a Slater determinant $|\Psi_{\text{S}}[n]\rangle$, and we define the functional

$$T_{\text{S}}[n] \equiv \min_{|\Psi_{\text{S}}\rangle \to n(\boldsymbol{x})}\big\langle\,\Psi_{\text{S}}[n]\,|\,\hat{T}\,|\,\Psi_{\text{S}}[n]\,\big\rangle \quad, \tag{8.88}$$

where $|\Psi_{\text{S}}\rangle$ is an $N$-particle Slater determinant. We may write

$$n(\boldsymbol{x}) = \sum_\alpha \sum_\sigma n_\alpha\,\big|\varphi_\alpha(\boldsymbol{x},\sigma)\big|^2 \quad, \tag{8.89}$$

where $n_\alpha \in \{0,1\}$ is the occupation of the single particle state $\varphi_\alpha(\boldsymbol{x},\sigma)$, with $N = \sum_\alpha n_\alpha$. We may write

$$T_{\text{S}}[n] = -\frac{\hbar^2}{2m}\sum_\alpha n_\alpha\,\langle\,\varphi_\alpha\,|\,\nabla^2\,|\,\varphi_\alpha\,\rangle \quad. \tag{8.90}$$

*Aside* – I want to comment yet again on the extremely complex and unusual nature of the functionals $E_{\text{jel}}[n]$ and $T_{\text{S}}[n]$. Functions, such as the iconic $f(x)$, eat numbers ($x \in \mathbb{R}$) and excrete numbers ($f(x) \in \mathbb{R}$). *Functionals*, such as $F[f(x)]$, by contrast eat entire *functions* ($f(x) \in C^\infty(\mathbb{R})$) and excrete numbers[7] ($F[f(x)] \in \mathbb{R}$). Usually it is the case that the functionals we deal with are specified explicitly. Such it is with the action functional in classical mechanics, $S[q(t)]$, where

$$S[q(t)] = \int\limits_{t_1}^{t_2} dt\, L(q,\dot{q},t) \tag{8.91}$$

[5] M. Levy, *Proc. Nat. Acad. Sci* **76**, 6062 (1979).
[6] E. H. Lieb, *Int. J. Quantum Chem.* **24**, 243 (1983).
[7] We can of course generalize to complex functions and complex functionals and functions of several variables $f(\boldsymbol{x}) \in C^\infty(\mathbb{R}^n)$.

with $L = \frac{1}{2}m\dot{q}^2 - V(q)$. In this case, if you give me the function $q(t)$, which typically must satisfy certain boundary conditions such as being fixed at the endpoints, I can in principle perform the above integral and hand you back $S[q(t)]$. Things are not so straightforward with regard to $T_S[n]$ and $E_{jel}[n]$. Rather, the prescriptions are as follows:

- For $T_S[n]$, you give me some function $n(\boldsymbol{x}) \in C^\infty(\mathbb{R}^d)$ and I rummage through my file cabinet of $N$-particle Slater determinant wavefunctions $\Psi_S(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N) = \det\{\varphi_{\alpha_i}(\boldsymbol{x}_j)\}$ constructed from inequivalent orthonormal bases, and I set aside only those functions for which the density $\langle \Psi_S | \hat{n}(\boldsymbol{x}) | \Psi_S \rangle = n(\boldsymbol{x})$ agrees with your specified function. Then, one-by-one, I go through this collection, computing $\langle \Psi_S | \hat{T} | \Psi_S \rangle$ for each, and I find which $\Psi_S$ yields the lowest expectation value, which is then the value of $T_S[n]$.

- For $E_{jel}[n]$, you give me a function $n(\boldsymbol{x})$, and I along with a bunch of volunteers search my giant warehouse of totally antisymmetric $N$-particle functions $\Psi(\boldsymbol{x}_1, \ldots, \boldsymbol{x}_N)$ for those $\Psi$ yielding $\langle \Psi | \hat{n}(\boldsymbol{x}) | \Psi \rangle = n(\boldsymbol{x})$.[8] For each of these surviving wavefunctions, we evaluate $\langle \Psi | \hat{T} + \hat{U} | \Psi \rangle$ and find which $\Psi$ yields the lowest expectation value. This is then the value of $E_{jel}[n]$.

As you can see, $T_S[n]$ and $E_{jel}[n]$ are indeed functionals of $n(\boldsymbol{x})$, because there is an explicit, if impractical, prescription for how they may be evaluated. Turning the evaluation of $E_{jel}[n]$ into an implementable variational scheme was the genius of Kohn and Sham, to whose program we now return.

Having defined the functionals $E_{jel}[n]$ and $T_S[n]$, we next define the *exchange-correlation functional* $E_{XC}[n]$ according to the relation

$$E_{jel}[n] = T_S[n] + E_H[n] + E_{XC}[n] \quad , \tag{8.92}$$

where $E_H[n]$ is the Hartree functional,

$$E_H[n] = \frac{1}{2} \int d^3x \int d^3x' \left(n(\boldsymbol{x}) - n_0\right) \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} \left(n(\boldsymbol{x}') - n_0\right) \quad . \tag{8.93}$$

Note that Eqn. 8.92 is a definition of the functional $E_{XC}[n]$ in terms of the universal functionals $E_{jel}[n]$ (which exists but is unknown), $E_H[n]$ (which is explicitly given in Eqn. 8.93), and $T_S[n]$ (which is given in Eqn. 8.90). Note that $T_S[n]$ is the kinetic energy of a fictional noninteracting fermion system which has the same density $n(\boldsymbol{x})$ as the interacting system under consideration.

*At this point, rather than vary with respect to $n(\boldsymbol{x})$, we instead vary with respect to each of the single particle wavefunctions $\varphi_\alpha^*(\boldsymbol{x}, \sigma)$, subject to the conditions of orthonormality.*

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[8]This is of course vastly bigger than my file cabinet of Slater determinants, a copy of which is stored somewhere in the warehouse, since $\{\Psi_S | \langle \Psi_S | \hat{n} | \Psi_S \rangle = n\} \in \{\Psi | \langle \Psi | \hat{n} | \Psi \rangle = n\}$.

This results in the Kohn-Sham equations,

$$\left\{ -\frac{\hbar^2}{2m} \nabla^2 + v_{\text{ext}}(\boldsymbol{x}) + v_{\text{H}}(\boldsymbol{x}) + v_{\text{XC}}(\boldsymbol{x}) \right\} \varphi_\alpha(\boldsymbol{x}, \sigma) = \varepsilon_\alpha \, \varphi_\alpha(\boldsymbol{x}, \sigma) \quad , \tag{8.94}$$

where $n_\alpha = 1$,

$$v_{\text{H}}(\boldsymbol{x}) = \frac{\delta E_{\text{H}}[n]}{\delta n(\boldsymbol{x})} = \int d^3 x' \, \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} \left( n(\boldsymbol{x}') - n_0 \right) \tag{8.95}$$

and where

$$v_{\text{XC}}(\boldsymbol{x}) = \frac{\delta E_{\text{XC}}[n]}{\delta n(\boldsymbol{x})} \tag{8.96}$$

are functional derivatives. Note that we have used the functional chain rule,

$$\frac{\delta F[n]}{\delta \varphi_\alpha^*(\boldsymbol{x})} = \frac{\delta F[n]}{\delta n(\boldsymbol{x})} \cdot \frac{\delta n(\boldsymbol{x})}{\delta \varphi_\alpha^*(\boldsymbol{x})} = \frac{\delta F[n]}{\delta n(\boldsymbol{x})} \, \varphi_\alpha(\boldsymbol{x}) \tag{8.97}$$

for any functional $F[n]$. Note that $v_{\text{XC}}(\boldsymbol{x})$ is local, unlike in Hartree-Fock theory where the Fock potential $v_{\text{F}}(\boldsymbol{x}, \boldsymbol{x}')$ is nonlocal.

It is worth emphasizing that while the Kohn-Sham orbitals $\varphi_\alpha(\boldsymbol{x}, \sigma)$ have no obvious physical significance, they are often interpreted as Bloch energy bands for the interacting system (whatever that means!). The KS eigenvalues $\varepsilon_\alpha$ do not in general correspond to physical excitation energies of the system, and the Slater determinant formed from the $N$ lowest-lying KS orbitals is in general *not* a good approximation to the actual ground state wavefunction. Indeed the HF wavefunction is often a better approximation in that regard. However, in the $N \to \infty$ limit, it can be proven[9] that in gapless systems the eigenvalue $\varepsilon_N$ corresponding to the highest occupied KS energy state is indeed the actual Fermi energy of the system.

At this point, the problem has been reduced to finding the best approximation to the unknown functional $E_{\text{XC}}[n]$.

**LDA: the local density approximation**

The most commonly used such approximation is called the *local density approximation*, or LDA. One writes

$$E_{\text{XC}}^{\text{LDA}} = \int d^3 x \, n(\boldsymbol{x}) \, \varepsilon_{\text{XC}}\big(n(\boldsymbol{x})\big) \quad . \tag{8.98}$$

The quantity $\varepsilon_{\text{XC}}\big(n(\boldsymbol{x})\big)$ is the exchange-correlation energy per particle for uniform density jellium. Taking the functional derivative,

$$\mu_{\text{XC}}\big(n(\boldsymbol{x})\big) = \frac{\delta E_{\text{XC}}^{\text{LDA}}}{\delta n(\boldsymbol{x})} = \varepsilon_{\text{XC}}\big(n(\boldsymbol{x})\big) + n(\boldsymbol{x}) \left. \frac{\partial \varepsilon_{\text{XC}}(n)}{\partial n} \right|_{n(\boldsymbol{x})} \quad . \tag{8.99}$$

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[9]G. Giuliani and G. Vignali, *op cit.*

Recall how in the HF approximation in $d = 3$, $E_{\mathsf{X}}/V = -(3e^2/4\pi)\, n k_{\mathrm{F}} \propto n^{4/3}$, hence

$$\mu_{\mathsf{XC}}(n) = \tfrac{4}{3}\, \varepsilon_{\mathsf{XC}}(n) = -\frac{e^2 k_{\mathrm{F}}(n)}{\pi} \quad , \tag{8.100}$$

where $k_{\mathrm{F}}(n) = (3\pi^2 n)^{1/3}$.

**Gradient expansions**

If we expand about the jellium density $n_0$, we may write

$$E_{\mathsf{XC}}^{\mathsf{GEA}}[n_0 + \delta n] = \frac{1}{2}\int d^3x \left\{ A(n_0)\,[\delta n(\boldsymbol{x})]^2 + B(n_0)\,[\boldsymbol{\nabla}\delta n(\boldsymbol{x})]^2 + \dots \right\} \quad . \tag{8.101}$$

This procedure goes under the name *gradient expansion approximation*, or GEA[10]. One can also define spin-resolved expansions *viz.*

$$E_{\mathsf{XC}}^{\mathsf{SGEA}}[n_{0\uparrow} + \delta n_\uparrow, n_{0\downarrow} + \delta n_\downarrow] = \frac{1}{2}\int d^3x \left\{ A_{\sigma\sigma'}(n_{0\uparrow}, n_{0\downarrow})\, \delta n_\sigma(\boldsymbol{x})\, \delta n_{\sigma'}(\boldsymbol{x}) \right. \tag{8.102}$$

$$\left. + B_{\sigma\sigma'}(n_{0\uparrow}, n_{0\downarrow})\, \boldsymbol{\nabla}\delta n_\sigma(\boldsymbol{x}) \cdot \boldsymbol{\nabla}\delta n_{\sigma'}(\boldsymbol{x}) + \dots \right\} \quad .$$

Alas, in applications to real materials, the GEA is often less accurate than the LDA.

**Major applications of DFT**

Girvin and Yang provide a brief list of popular applications of DFT. For each such application there are many thousands of papers in the literature:

- *Structural determination* : Given a set of atoms, what sort of crystal structure will they form? The external potential is given by

$$v_{\mathsf{ext}}(\boldsymbol{x}) = -\sum_l \frac{Z_l\, e^2}{|\boldsymbol{R}_l - \boldsymbol{x}|} \quad . \tag{8.103}$$

The total energy is then

$$E_{\mathsf{tot}}\big[\{\boldsymbol{R}_l\}, n(\boldsymbol{x})\big] = E_{\mathsf{jel}}[n] + \int d^3x\, n(\boldsymbol{x})\, v_{\mathsf{ext}}(\boldsymbol{x}) + \sum_{l<l'} \frac{Z_l\, Z_{l'}\, e^2}{|\boldsymbol{R}_l - \boldsymbol{R}_{l'}|} \quad . \tag{8.104}$$

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[10]Density functional theory is replete with acronyms.

For a given set of nuclear positions $\{\boldsymbol{R}_l\}$, the energy functional is minimized with respect to the density $n(\boldsymbol{x})$. The resulting energy is then a function of the nuclear positions, and is then minimized with respect to these variables, yielding the crystal structure. Typically one works with periodic boundary conditions and with as large a crystallite cell as one can computationally afford in order to approximate the thermodynamic limit.

- *Cohesive energy* : The difference between the minimum energy per unit cell in the crystalline state and the total atomic energy of each atom in the unit cell is called the *cohesive energy* $E_{\text{coh}} = E_{\text{crystal}} - E_{\text{atomic}}$. If $E_{\text{coh}} < 0$, then crystal formation is advantageous, and the difference is the crystalline *binding energy* per unit cell.

- *Elastic constants* : After the optimal crystalline structure is determined, by varying with respect to the nuclear positions one can obtain the elastic constants.

- *Phase diagram under pressure* : At $T = 0$ the Gibbs free energy $G = E - TS + pV$ is the enthalpy $H = E + pV$. Including the $pV$ term in the energy, one can evaluate the $T = 0$ Gibbs free energy at any finite pressure.

## 8.4   Response Functions

### 8.4.1   Linear response theory

What can we do with $E_{\text{jel}}[n]$? For starters, we can compute response functions for the jellium system. If the uniform density for pure jellium is $n_0$, then upon introducing a potential $v_{\text{ext}}(\boldsymbol{x})$ we may write $n(\boldsymbol{x}) = n_0 + \delta n(\boldsymbol{x})$. Expanding the functional $E_{\text{jel}}[n]$ about $n = n_0$, we have that the total energy functional $E[n] = E_{\text{jel}}[n] + V[n]$, to second order in $\delta n$, is given by

$$E[n_0 + \delta n] = E_{\text{jel}}[n_0] + \frac{1}{2} \int d^3x \int d^3x' \left. \frac{\delta E_{\text{jel}}[n]}{\delta n(\boldsymbol{x})\,\delta n(\boldsymbol{x}')} \right|_{n_0} \delta n(\boldsymbol{x})\,\delta n(\boldsymbol{x}') + \int d^3x \left( n_0 + \delta n(\boldsymbol{x}) \right) v_{\text{ext}}(\boldsymbol{x}) \quad .$$

(8.105)

Note that the first functional variation $\delta E_{\text{jel}}[n_0] = 0$ vanishes for $n = n_0$ by definition. Thus,

$$\left. \frac{\delta E[n]}{\delta n(\boldsymbol{x})} \right|_{n_0} = v_{\text{ext}}(\boldsymbol{x}) + \int d^3x' \, \chi^{-1}(\boldsymbol{x}, \boldsymbol{x}')\, \delta n(\boldsymbol{x}') \quad , \tag{8.106}$$

where[11]

$$\chi^{-1}(\boldsymbol{x}, \boldsymbol{x}') \equiv \left. \frac{\delta^2 E_{\text{jel}}[n]}{\delta n(\boldsymbol{x})\,\delta n(\boldsymbol{x}')} \right|_{n_0} \quad . \tag{8.107}$$

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[11]Note that this definition differs by a minus sign by that in ch. 15 of Girvin and Yang, *Modern Condensed Matter Physics*.

The function $\chi^{-1}(\boldsymbol{x}, \boldsymbol{x}')$ is the inverse density susceptibility. The relation between $\chi^{-1}$ and $\chi$ is

$$\int d^3x' \, \chi^{-1}(\boldsymbol{x}, \boldsymbol{x}') \, \chi(\boldsymbol{x}', \boldsymbol{x}'') = \delta(\boldsymbol{x} - \boldsymbol{x}'') \quad , \tag{8.108}$$

thus Eqn. 8.106 is equivalent to

$$\delta n(\boldsymbol{x}) = - \int d^3x' \, \chi(\boldsymbol{x}, \boldsymbol{x}') \, v_{\text{ext}}(\boldsymbol{x}') \quad . \tag{8.109}$$

The above formula is an example of *linear response*. Had we expanded $E[n_0 + \delta n]$ to higher order in $\delta n$, we'd have obtained higher order terms on the RHS, arranged as a functional Taylor series in $v_{\text{ext}}(\boldsymbol{x})$.

Since the jellium system is translationally invariant, we must have $\chi(\boldsymbol{x}, \boldsymbol{x}') = \chi(\boldsymbol{x} - \boldsymbol{x}')$. We now define the Fourier transform $\hat{\chi}(\boldsymbol{q})$ as

$$\hat{\chi}(\boldsymbol{q}) \equiv \int d^dx \, \chi(\boldsymbol{x}) \, e^{-i\boldsymbol{q}\cdot\boldsymbol{x}} \quad , \tag{8.110}$$

where $d = 3$ in the present discussion. The FT of $\chi^{-1}(\boldsymbol{x} - \boldsymbol{x}')$ is $\hat{\chi}^{-1}(\boldsymbol{q}) = 1/\hat{\chi}(\boldsymbol{q})$. Thus, within linear response,

$$\delta\hat{n}(\boldsymbol{q}) = -\hat{\chi}(\boldsymbol{q}) \, \hat{v}_{\text{ext}}(\boldsymbol{q}) \quad . \tag{8.111}$$

We write, as above,

$$E[n] = T_{\mathsf{S}}[n] + V[n] + E_{\mathsf{H}}[n] + E_{\mathsf{XC}}[n] \quad . \tag{8.112}$$

We define the noninteracting susceptibility according to

$$\chi_0^{-1}(\boldsymbol{x}, \boldsymbol{x}') = \frac{\delta^2 T_{\mathsf{S}}[n]}{\delta n(\boldsymbol{x}) \, \delta n(\boldsymbol{x}')}\bigg|_{n_0} = \frac{1}{V} \sum_{\boldsymbol{q}} \hat{\chi}_0^{-1}(\boldsymbol{q}) \, e^{i\boldsymbol{q}\cdot(\boldsymbol{x}-\boldsymbol{x}')} \quad , \tag{8.113}$$

where, as we shall derive later,

$$\hat{\chi}_0(\boldsymbol{q}) = 2 \int \frac{d^dk}{(2\pi)^d} \, \frac{f^0(\boldsymbol{k}+\boldsymbol{q}) - f^0(\boldsymbol{k})}{\varepsilon_0(\boldsymbol{k}) - \varepsilon_0(\boldsymbol{k}+\boldsymbol{q})} \quad , \tag{8.114}$$

where $\varepsilon_0(\boldsymbol{k}) = \hbar^2\boldsymbol{k}^2/2m$ is the noninteracting dispersion, and

$$f^0(\boldsymbol{k}) = \frac{1}{\exp\left(\frac{\varepsilon_0(\boldsymbol{k})-\mu}{k_{\mathrm{B}}T}\right) + 1} \tag{8.115}$$

is the Fermi distribution. At $T = 0$, we have $f^0(\boldsymbol{k}) = \Theta(k_{\mathrm{F}} - k)$. Performing the integral in $d = 3$ dimensions, we obtain

$$\hat{\chi}_0(\boldsymbol{q}, T = 0) = g(\varepsilon_{\mathrm{F}}) \, L(q/2k_{\mathrm{F}}) \quad , \tag{8.116}$$

where $g(\varepsilon_{\rm F}) = mk_{\rm F}/\pi^2\hbar^2$ is the DOS at the Fermi level, with $k_{\rm F}(n) = (3\pi^2 n)^{1/3}$, and where

$$L(x) = \frac{1}{2} + \frac{1-x^2}{4x} \ln\left|\frac{1+x}{1-x}\right| \tag{8.117}$$

is the *Lindhard function*. We may now write

$$\chi^{-1}(\boldsymbol{x}, \boldsymbol{x}') = \chi_0^{-1}(\boldsymbol{x}, \boldsymbol{x}') + \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} + \chi_{\rm XC}^{-1}(\boldsymbol{x}, \boldsymbol{x}') \tag{8.118}$$

where

$$\chi_{\rm XC}^{-1}(\boldsymbol{x}, \boldsymbol{x}') = \left.\frac{\delta^2 E_{\rm XC}[n]}{\delta n(\boldsymbol{x})\,\delta n(\boldsymbol{x}')}\right|_{n_0} . \tag{8.119}$$

Note that

$$\chi_{\rm H}^{-1}(\boldsymbol{x}, \boldsymbol{x}') = \left.\frac{\delta^2 E_{\rm H}[n]}{\delta n(\boldsymbol{x})\,\delta n(\boldsymbol{x}')}\right|_{n_0} = \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|} . \tag{8.120}$$

Assuming translational invariance, $\chi_a(\boldsymbol{x}, \boldsymbol{x}') = \chi_a(\boldsymbol{x} - \boldsymbol{x}')$ for all labels $a$ (*e.g.*, $\chi$, $\chi_0$, $\chi_{\rm H}$, $\chi_{\rm XC}$), and $\chi_a^{-1}(\boldsymbol{x}, \boldsymbol{x}') = \chi_a^{-1}(\boldsymbol{x} - \boldsymbol{x}')$ as well. Taking the Fourier transforms, then, we obtain

$$\hat{\chi}^{-1}(\boldsymbol{q}) = \hat{\chi}_0^{-1}(\boldsymbol{q}) + \frac{4\pi e^2}{\boldsymbol{q}^2} + \hat{\chi}_{\rm XC}^{-1}(\boldsymbol{q}) \equiv \widehat{\Pi}^{-1}(\boldsymbol{q}) + \frac{4\pi e^2}{\boldsymbol{q}^2} , \tag{8.121}$$

where the inverse of the *polarization function* $\widehat{\Pi}(\boldsymbol{q})$ is defined according to

$$\widehat{\Pi}^{-1}(\boldsymbol{q}) = \hat{\chi}_0^{-1}(\boldsymbol{q}) + \hat{\chi}_{\rm XC}^{-1}(\boldsymbol{q}) . \tag{8.122}$$

## 8.4.2  Static screening

We conclude that in the presence of an external potential $v_{\rm ext}(\boldsymbol{x})$, there is to first order a density response $\delta\hat{n}(\boldsymbol{q}) = -\hat{\chi}(\boldsymbol{q})\,\hat{v}_{\rm ext}(\boldsymbol{q})$. The corresponding charge profile is then $\delta\hat{\varrho}(\boldsymbol{q}) = -e\,\delta\hat{n}(\boldsymbol{q})$. Hence the potential is *screened*. Within linear response, this results in an effective screened potential

$$v_{\rm scr}(\boldsymbol{x}) = v_{\rm ext}(\boldsymbol{x}) + \int d^3x'\, \frac{e^2}{|\boldsymbol{x} - \boldsymbol{x}'|}\,\delta n(\boldsymbol{x}')$$

$$\hat{v}_{\rm scr}(\boldsymbol{q}) = \hat{v}_{\rm ext}(\boldsymbol{q}) - \frac{4\pi e^2}{\boldsymbol{q}^2}\,\hat{\chi}(\boldsymbol{q})\,\hat{v}_{\rm ext}(\boldsymbol{q}) \equiv \frac{\hat{v}_{\rm ext}(\boldsymbol{q})}{\hat{\epsilon}(\boldsymbol{q})} , \tag{8.123}$$

where $\hat{\epsilon}(\boldsymbol{q})$ is the static (*i.e.* zero frequency) *dielectric constant*, given. by

$$\hat{\epsilon}^{-1}(\boldsymbol{q}) = 1 - \frac{4\pi e^2}{\boldsymbol{q}^2}\,\hat{\chi}(\boldsymbol{q})$$

$$= 1 - \frac{4\pi e^2/\boldsymbol{q}^2}{\widehat{\Pi}^{-1}(\boldsymbol{q}) + 4\pi e^2/\boldsymbol{q}^2} = \frac{1}{1 + \frac{4\pi e^2}{\boldsymbol{q}^2}\,\widehat{\Pi}(\boldsymbol{q})} . \tag{8.124}$$

Thus,

$$\hat{\epsilon}(\boldsymbol{q}) = 1 + \frac{4\pi e^2}{\boldsymbol{q}^2}\,\widehat{\Pi}(\boldsymbol{q}) \quad . \tag{8.125}$$

If we ignore the $\boldsymbol{q}$-dependence and approximate $\widehat{\Pi}(\boldsymbol{q}) \approx \widehat{\Pi}(0) \equiv Q^2/4\pi e^2$, which defines a quantity $Q$ with dimensions of inverse length, then

$$\hat{\epsilon}(\boldsymbol{q}) \approx 1 + \frac{Q^2}{\boldsymbol{q}^2} \tag{8.126}$$

and for $v_{\text{ext}}(\boldsymbol{r}) = -Ze^2/r$, we have $\hat{v}_{\text{ext}}(\boldsymbol{q}) = -4\pi Ze^2/\boldsymbol{q}^2$ and the FT of the screened potential is

$$\hat{v}_{\text{scr}}(\boldsymbol{q}) = -\frac{4\pi Ze^2}{\boldsymbol{q}^2 + Q^2} \quad , \tag{8.127}$$

which in real space $(d = 3)$ corresponds to a Yukawa potential,

$$v_{\text{scr}}(\boldsymbol{r}) = -\frac{Ze^2 \exp(-Qr)}{r} \quad . \tag{8.128}$$

Thus, the screened potential is much weaker at long distances (exponentially so) than the bare $1/r$ Coulomb potential.

Note that the total number of electrons accumulated within linear response theory is

$$\delta N = \int d^3x\,\delta n(\boldsymbol{x}) = -\lim_{\boldsymbol{q}\to 0}\,\hat{\chi}(\boldsymbol{q})\,\hat{v}_{\text{ext}}(\boldsymbol{q})$$
$$= \lim_{\boldsymbol{q}\to 0}\frac{Z}{1 + (\boldsymbol{q}^2/4\pi e^2)\,\widehat{\Pi}^{-1}(\boldsymbol{q})} \quad . \tag{8.129}$$

Thus, provided $\boldsymbol{q}^2/\widehat{\Pi}(\boldsymbol{q})$ vanishes in the limit $\boldsymbol{q} \to 0$, we obtain *perfect screening* by an induced charge $Q = -e\,\delta N = -Ze$ of the charge $+Ze$ impurity.

We emphasize that throughout this section we are discussing only the linear response of the jellium system. To compute the linear response of a material like elemental Pb, say, we'd need to solve the KS equations and evaluate the various functional derivatives at a number density $n(\boldsymbol{x})$ which is the ground state electron density for Pb.

### 8.4.3   Approximate forms for the polarization function

The static dielectric function $\hat{\epsilon}(\boldsymbol{q})$ is given to us, in Eqn. 8.125, in terms of the unknown polarization function $\widehat{\Pi}(\boldsymbol{q})$. There are two common approximations we shall discuss here.

The first is the *Lindhard approximation*, in which we ignore $\hat{\chi}_{\text{XC}}(\boldsymbol{q})$ and write $\widehat{\Pi}(\boldsymbol{q}) \approx \widehat{\Pi}_{\text{L}}(\boldsymbol{q})$ where $\widehat{\Pi}_{\text{L}}(\boldsymbol{q}) = \hat{\chi}_0(\boldsymbol{q})$, which is given in Eqns. 8.116 and 8.117 above. Thus

$$\hat{\chi}(\boldsymbol{q}) \approx \hat{\chi}_{\text{L}}(\boldsymbol{q}) \equiv \frac{\hat{\chi}_0(\boldsymbol{q})}{1 + \frac{4\pi e^2}{\boldsymbol{q}^2}\,\hat{\chi}_0(\boldsymbol{q})} \quad , \qquad \hat{\epsilon}(\boldsymbol{q}) \approx \hat{\epsilon}_{\text{L}}(\boldsymbol{q}) \equiv 1 + \frac{4\pi e^2}{\boldsymbol{q}^2}\,\hat{\chi}_0(\boldsymbol{q}) \quad . \tag{8.130}$$

In the $q \to 0$ limit, $\widehat{\sqcap}_{\mathsf{L}}(q) = g(\varepsilon_{\mathsf{F}}) + \mathcal{O}(q^2)$, which entails perfect screening of a Coulomb impurity, *i.e.* $\delta N = Z$. However, rather than obtaining a Yukawa form for the screened potential, one instead finds

$$v_{\mathsf{scr}}(\boldsymbol{r}) \propto \frac{\cos(2k_{\mathsf{F}}r)}{r^3} \tag{8.131}$$

in the long distance limit. This arises from the logarithmic singularity in the Lindhard function $L(q/2k_{\mathsf{F}})$ (Eqn. 8.117) at $q = 2k_{\mathsf{F}}$, which is a feature of the sharp Fermi surface.

A further simplification is the *Thomas-Fermi* (new acronym: TF) approximation, in which we also ignore the $q$-dependence and write $\widehat{\sqcap}(q) \approx \widehat{\sqcap}_{\mathsf{L}}(0) = g(\varepsilon_{\mathsf{F}}) \equiv Q_{\mathsf{TF}}^2/4\pi e^2$, where $Q_{\mathsf{TF}} = \sqrt{4\pi e^2 g(\varepsilon_{\mathsf{F}})}$ is the TF wavevector. Thus $\hat{\epsilon}_{\mathsf{TF}}(q) = 1 + \frac{Q_{\mathsf{TF}}^2}{q^2}$ and the screened potential is of the Yukawa form. For a quick and dirty way to derive TF theory, assume that the electric potential $\phi(\boldsymbol{x})$ varies slowly in space, and imagine locally shifting the Fermi energy by the local electrostatic energy, *i.e.* from $\varepsilon_{\mathsf{F}}$ to $\varepsilon_{\mathsf{F}} + e\,\phi(\boldsymbol{x})$. This results in a local density accumulation $\delta n(\boldsymbol{x}) = e\,\phi(\boldsymbol{x})\,g(\varepsilon_{\mathsf{F}})$, and invoking Poisson's equation,

$$\nabla^2\phi = -4\pi\varrho = 4\pi e\,\delta n = 4\pi e^2 g(\varepsilon_{\mathsf{F}})\,\phi = Q_{\mathsf{TF}}^2\,\phi \quad , \tag{8.132}$$

whence the Yukawa potential. By ignoring the $q$-dependence, we have missed the Fermi surface singularity which is present in the (more realistic) Lindhard approximation. Note that the TF wavelength, $\lambda_{\mathsf{TF}} = Q_{\mathsf{TF}}^{-1}$, is given by

$$\lambda_{\mathsf{TF}} = \left(\frac{\pi}{12}\right)^{1/6} \sqrt{r_{\mathsf{s}}}\,a_{\mathsf{B}} \approx 0.800\,\sqrt{r_{\mathsf{s}}}\,a_{\mathsf{B}} \quad . \tag{8.133}$$

Recall that $\frac{4}{3}\pi(r_{\mathsf{s}}\,a_{\mathsf{B}})^3 n \equiv 1$ defines $r_{\mathsf{s}}$, hence $r_{\mathsf{s}} \propto n^{-1/3}$. TF theory is statistical and can only be justified if there are a large number of electrons within a sphere of radius $\lambda_{\mathsf{TF}}$, which says $r_{\mathsf{s}} \lesssim (\pi/12)^{1/3} \simeq 0.640$.

There is another kind of screening in solids which is relevant when the temperature is much larger than the Fermi energy. This is called Debye-Hückel screening and the argument goes as follows. Let the background charge density be $\varrho_0 = e\,n_0$. Classical statistical physics then yields a local electron density $n(\boldsymbol{x}) = n_0 \exp\big[e\phi(\boldsymbol{x})/k_{\mathsf{B}}T\big]$, and invoking Poisson results in the equation $\nabla^2\phi = Q_{\mathsf{DH}}^2\,\phi$, where $Q_{\mathsf{DH}} = \sqrt{k_{\mathsf{B}}T/4\pi n_0 e^2}$.