

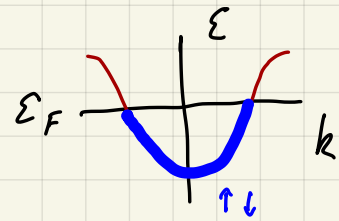
• Nernst effect  $\vec{j} = \partial_y T = 0$

$$\vec{\nabla}T = \partial_x T \hat{x} \text{ and } \vec{B} = B_z \hat{z} \Rightarrow \mathcal{E}_y = \Lambda \partial_x T B_z \text{ with } \Lambda = -c$$

• Righi-Leduc effect  $\vec{j} = \mathcal{E}_y = 0$

$$\vec{\nabla}T = \partial_x T \hat{x} \text{ and } \vec{B} = B_z \hat{z} \Rightarrow \partial_y T = \mathcal{L} \partial_x T B_z \text{ with } \mathcal{L} = c/Q$$

• Lecture 7 (Jan. 26)



## Interacting electrons

Thus far we have mainly discussed noninteracting electrons. Other than a brief introduction to screening, we've accounted for many-body effects mainly via Pauli exclusion. This is what requires that we fill single particle levels at  $T=0$  up to the Fermi level  $\epsilon_F$ , with all states  $|\alpha\rangle$  with  $\epsilon_\alpha > \epsilon_F$  unoccupied. The many-body wavefunction for such a state is a Slater determinant,

$$\Psi_{\alpha_1, \dots, \alpha_N}(\vec{r}_1, \sigma_1, \dots, \vec{r}_N, \sigma_N) = \det\{\varphi_{\alpha_i}(\vec{r}_j, \sigma_j)\} \begin{cases} \alpha_i = (k_i, \zeta_i) \\ \eta_\zeta(\sigma) = \delta_{\sigma\zeta} \end{cases}$$

which satisfies the total antisymmetry condition  $\pi \in S_N$

$$\Psi_{\alpha_1, \dots, \alpha_N}(\vec{r}_{\pi(1)}, \sigma_{\pi(1)}, \dots, \vec{r}_{\pi(N)}, \sigma_{\pi(N)}) = \text{sgn}(\pi) \Psi_{\alpha_1, \dots, \alpha_N}(\vec{r}_1, \sigma_1, \dots, \vec{r}_N, \sigma_N)$$

Thus if  $(\vec{r}_i, \sigma_i) = (\vec{r}_j, \sigma_j)$  for some  $i \neq j$ , then  $\Psi = 0$ .

But Slater determinants are only a subset of fermionic

many-body WFs which exhibit total antisymmetry. Clearly an arbitrary linear combination of Slater determinants also is totally antisymmetric.

$$|\Psi\rangle = \overset{\text{FFS}}{\text{M}} + \text{M} + \dots$$

## • Second quantization

Second quantization is a convenient notational scheme for labeling basis states of quantum many-body systems. Suppose we have an orthonormal single particle basis  $\varphi_\alpha(\vec{x})$ , where we include in the position  $\vec{x}$  any internal labels, such as spin polarization. Thus  $\varphi_\alpha(\vec{x}) = \langle \vec{x} | \alpha \rangle$  and  $\langle \alpha | \alpha' \rangle = \delta_{\alpha\alpha'}$ .

We define the  $N$ -body state

$$\Psi_{\alpha_1 \dots \alpha_N}(\vec{x}_1, \dots, \vec{x}_N) = \frac{1}{\sqrt{N! \prod_\alpha n_\alpha!}} \sum_{\pi \in S_N} \left\{ \overset{\text{BE}}{\underset{\text{FD}}{\text{sgn}(\pi)}} \right\} \varphi_{\alpha_1}(\vec{x}_{\pi(1)}) \dots \varphi_{\alpha_N}(\vec{x}_{\pi(N)})$$

The upper sign is for bosons and the lower sign for fermions.

$n_\alpha$  is the number of times the label  $\alpha$  appears in  $\{\alpha_1, \dots, \alpha_N\}$ .

Only  $n_\alpha \in \{0, 1\}$  are allowed for fermions, else  $\Psi_\alpha(\vec{X}) = 0$ .

Note that

$$\sum_{\pi \in S_N} \varphi_{\alpha_1}(\vec{x}_{\pi(1)}) \dots \varphi_{\alpha_N}(\vec{x}_{\pi(N)}) = \text{per} \{ \varphi_{\alpha_i}(\vec{x}_j) \} \quad \text{permanent}$$

$$\sum_{\pi \in S_N} \text{sgn}(\pi) \varphi_{\alpha_1}(\vec{x}_{\pi(1)}) \dots \varphi_{\alpha_N}(\vec{x}_{\pi(N)}) = \det \{ \varphi_i(\vec{x}_j) \} \quad \text{determinant}$$

The permanent and determinant wavefunctions constitute

bases for  $N$ -particle many body wave functions for bosons and fermions, respectively. An arbitrary linear combination

$$\Psi(\vec{x}_1, \dots, \vec{x}_N) = \sum_{\vec{\alpha}} C_{\alpha_1 \dots \alpha_N} \begin{cases} \text{per} \\ \text{det} \end{cases} \{ \varphi_{\alpha_i}(\vec{x}_j) \}$$

satisfies the condition

$$\Psi(\vec{x}_{\pi(1)}, \dots, \vec{x}_{\pi(N)}) = \text{sgn}(\pi) \Psi(\vec{x}_1, \dots, \vec{x}_N)$$

where  $\pi \in S_N$ . We may write

$$\Psi_{\alpha_1 \dots \alpha_N}(\vec{x}_1, \dots, \vec{x}_N) = \langle \vec{x}_1, \dots, \vec{x}_N | \alpha_1 \dots \alpha_N \rangle$$

where

$$|\alpha_1 \dots \alpha_N\rangle = \frac{1}{\sqrt{N! \prod_{\alpha} n_{\alpha}!}} \sum_{\pi \in S_N} \{ \text{sgn}(\pi) \} \underbrace{|\alpha_{\pi(1)}, \dots, \alpha_{\pi(N)}\rangle}_{\text{per/det}} \otimes \dots \otimes |\alpha_{\pi(N)}\rangle$$

Thus  $|\alpha_{\pi(1)} \dots \alpha_{\pi(N)}\rangle = (\pm 1)^{\pi} |\alpha_1 \dots \alpha_N\rangle$  where  $(\pm 1)^{\pi} \equiv \{ \text{sgn}(\pi) \}$   
and furthermore

$$\langle \alpha_1 \dots \alpha_N | \beta_1 \dots \beta_N \rangle = (\pm 1)^{\pi} \delta_{\beta_1, \alpha_{\pi(1)}} \dots \delta_{\beta_N, \alpha_{\pi(N)}}$$

for some  $\pi \in S_N$ .

Fock space operators:

For bosons, we write

$$|\alpha_1 \dots \alpha_N\rangle = \prod_{\alpha} \frac{(b_{\alpha}^{\dagger})^{n_{\alpha}}}{\sqrt{n_{\alpha}!}} |0\rangle \equiv |\{n_{\alpha}\}\rangle \quad ; \quad \sum_{\alpha} n_{\alpha} = N$$

Fock space vacuum (0 particles)

where  $|0\rangle$  is the boson vacuum. The total particle number is  $N = \sum_{\alpha} n_{\alpha}$ . The creation operators  $b_{\alpha}^{\dagger}$  and the annihilation operators  $b_{\alpha}$  satisfy the following commutation relations:

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

where  $[A, B] = AB - BA$ . We call  $\hat{n}_{\alpha} \equiv b_{\alpha}^{\dagger} b_{\alpha}$  the number operator. Exercise: show  $\hat{n}_{\alpha} |\alpha_1 \dots \alpha_N\rangle = n_{\alpha} |\alpha_1 \dots \alpha_N\rangle$ .

For fermions,

$$|\alpha_1 \dots \alpha_N\rangle = \prod_{\alpha} (c_{\alpha}^{\dagger})^{n_{\alpha}} |0\rangle = c_{\alpha_1}^{\dagger} \dots c_{\alpha_N}^{\dagger} |0\rangle \equiv |\{n_{\alpha}\}\rangle; \quad \sum_{\alpha} n_{\alpha} = N$$

where  $n_{\alpha} \in \{0, 1\} \forall \alpha$ . Thus  $n_{\alpha} = 1$  for  $\alpha \in \{\alpha_1, \dots, \alpha_N\}$  and  $n_{\alpha} = 0$  otherwise. (We implicitly assume a canonical ordering of the labels  $\alpha$  such that  $\alpha_1 < \alpha_2 < \dots < \alpha_N$ .) The fermionic creation and annihilation operators satisfy anticommutation relations:

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

where  $\{A, B\} = AB + BA$ . Note  $c_{\alpha_{\pi(1)}}^{\dagger} \dots c_{\alpha_{\pi(N)}}^{\dagger} |0\rangle = \text{sgn}(\pi) |\{n_{\alpha}\}\rangle$

We also define the field operators,

$$b(\vec{x}) = \sum_{\alpha} \varphi_{\alpha}(\vec{x}) b_{\alpha}, \quad c_{\alpha}(\vec{x}) = \sum_{\alpha} \varphi_{\alpha}(\vec{x}) c_{\alpha}$$

which satisfy

$$[b(\vec{x}), b^{\dagger}(\vec{x}')] = \delta(\vec{x} - \vec{x}'), \quad \{c_{\alpha}(\vec{x}), c_{\alpha}^{\dagger}(\vec{x}')\} = \delta(\vec{x} - \vec{x}')$$

We may define

$$\psi^\dagger(\vec{x}) = b^\dagger(\vec{x}) \text{ or } c^\dagger(\vec{x})$$

$$\underbrace{|\vec{x}_1 \dots \vec{x}_N\rangle}_{\text{all distinct}} \equiv \psi^\dagger(\vec{x}_1) \dots \psi^\dagger(\vec{x}_N) |0\rangle$$

$$= \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \left\{ \text{sgn}(\pi) \right\} |\vec{x}_{\pi(1)}, \dots, \vec{x}_{\pi(N)}\rangle$$

which differs from the state

$$|\vec{x}_1, \dots, \vec{x}_N\rangle = |\vec{x}_1\rangle \otimes \dots \otimes |\vec{x}_N\rangle$$

See Eqns. 8.19 and 8.20 in the lecture notes.

Second quantized Hamiltonian:

We assume  $\hat{H} = \hat{T} + \hat{V} + \hat{U}$ , where

$$\hat{T} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \vec{\nabla}_i^2, \quad \hat{V} = \sum_{i=1}^N v_{\text{ext}}(\vec{x}_i), \quad \hat{U} = \sum_{i < j} u(\vec{x}_i - \vec{x}_j)$$

kinetic energy                      external potential                      two-body interactions

We call  $\hat{t} \equiv -\frac{\hbar^2}{2m} \vec{\nabla}^2$ . We may represent  $\hat{T}$ ,  $\hat{V}$ , and  $\hat{U}$  in second quantized notation as:

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

$$\hat{N} = \sum_\alpha \psi_\alpha^\dagger \psi_\alpha$$

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

$$[\hat{N}, \hat{T}] = [\hat{N}, \hat{V}] = [\hat{N}, \hat{U}] = 0$$

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

total particle number is "good quantum number"

where

$$\langle \alpha | \hat{t} | \beta \rangle = \int d^d x \varphi_\alpha^*(\vec{x}) t(\vec{\nabla}) \varphi_\beta(\vec{x}) \equiv \tau_{\alpha\beta}$$

$$\langle \alpha | \hat{v}_{\text{ext}} | \beta \rangle = \int d^d x \varphi_\alpha^*(\vec{x}) v_{\text{ext}}(\vec{x}) \varphi_\beta(\vec{x}) \equiv v_{\alpha\beta}^{\text{ext}}$$

$$\langle \alpha\beta | \hat{u} | \gamma\delta \rangle = \int d^d x \int d^d x' \varphi_\alpha^*(\vec{x}) \varphi_\beta^*(\vec{x}') u(\vec{x}-\vec{x}') \varphi_\gamma(\vec{x}') \varphi_\delta(\vec{x}) \equiv u_{\alpha\beta\gamma\delta}$$

This may be generalized to  $n$ -body operators.

For a Hamiltonian consisting solely of one-body operators, we have

$$\hat{H} = \sum_{\alpha, \beta} (\tau_{\alpha\beta} + v_{\alpha\beta}^{\text{ext}}) \psi_\alpha^\dagger \psi_\beta$$

We may then make a unitary transformation  $\psi_\alpha = U_{\alpha a} \chi_a$  with  $U_{a\alpha}^\dagger (\tau_{\alpha\beta} + v_{\alpha\beta}^{\text{ext}}) U_{\beta b} = \epsilon_a \delta_{ab}$ , in which case

$$\hat{H} = \sum_a \epsilon_a \chi_a^\dagger \chi_a$$

Example:  $\hat{H} = -\frac{\hbar^2}{2m} \vec{\nabla}^2 + V(\vec{r})$  with  $V(\vec{r} + \vec{R}) = V(\vec{r})$ .

Then

$$\hat{H} = \sum_n \sum_{\vec{k} \in \hat{\Omega}} \sum_{\sigma} E_n(\vec{k}) \chi_{n\vec{k}\sigma}^\dagger \chi_{n\vec{k}\sigma}$$

← creates Bloch state  $|n\vec{k}\sigma\rangle$

### Hartree-Fock Theory:

Consider the interacting Hamiltonian,

$$\hat{H} = \sum_{i=1}^N \left\{ -\frac{\hbar^2}{2m} \vec{\nabla}_i^2 + v^{\text{ext}}(\vec{x}_i) \right\} + \sum_{i,j}^N u(\vec{x}_i - \vec{x}_j)$$

We seek to construct the best possible Slater determinant state,

$$\Psi(\vec{x}_1, \sigma_1, \dots, \vec{x}_N, \sigma_N) = \frac{1}{\sqrt{N!}} \sum_{\pi \in S_N} \text{sgn}(\pi) \prod_{i=1}^N \varphi_{\alpha_i}(\vec{x}_{\pi(i)}, \sigma_{\pi(i)})$$

In our second-quantized notation,

$$\hat{H} = \int d^d x \psi_{\sigma}^{\dagger}(\vec{x}) \left\{ -\frac{\hbar^2}{2m} \delta_{\sigma\tau} \vec{\nabla}^2 + V_{\sigma\tau}^{\text{ext}}(\vec{x}) \right\} \psi_{\tau}(\vec{x}) \\ + \frac{1}{2} \int d^d x \int d^d x' \psi_{\sigma}^{\dagger}(\vec{x}) \psi_{\sigma'}^{\dagger}(\vec{x}') u_{\sigma\tau\sigma'\tau'}(\vec{x}-\vec{x}') \psi_{\tau'}(\vec{x}') \psi_{\tau}(\vec{x})$$

Here,  $\{\sigma, \tau, \sigma', \tau'\}$  are spin polarizations. When we have spin isotropy, we may separate

$$u_{\sigma\tau\sigma'\tau'}(\vec{x}-\vec{x}') = u_0(\vec{x}-\vec{x}') \delta_{\sigma\tau} \delta_{\sigma'\tau'} + u_1(\vec{x}-\vec{x}') \underbrace{\vec{\sigma}_{\sigma\tau} \cdot \vec{\sigma}_{\sigma'\tau'}}_{\text{Heisenberg}}$$

We want the energy  $E = \langle \Psi | \hat{H} | \Psi \rangle$ , so we need

$$\begin{aligned} \bullet \langle \Psi | \psi_{\sigma}^{\dagger}(\vec{x}) \psi_{\tau}(\vec{x}') | \Psi \rangle &= \sum_{\alpha}^{\text{occ}} \varphi_{\alpha}^*(\vec{x}, \sigma) \varphi_{\alpha}(\vec{x}', \tau) \\ \bullet \langle \Psi | \psi_{\sigma}^{\dagger}(\vec{x}) \psi_{\sigma'}^{\dagger}(\vec{x}') \psi_{\tau'}(\vec{x}') \psi_{\tau}(\vec{x}) | \Psi \rangle &= \sum_{\alpha, \beta}^{\text{occ}} \varphi_{\alpha}^*(\vec{x}, \sigma) \varphi_{\beta}^*(\vec{x}', \sigma') \\ &\quad \times (\varphi_{\alpha}(\vec{x}, \tau) \varphi_{\beta}(\vec{x}', \tau') - \varphi_{\beta}(\vec{x}, \tau) \varphi_{\alpha}(\vec{x}', \tau')) \end{aligned}$$

Thus,

$$T = \langle \hat{T} \rangle = \sum_{\alpha}^{\text{occ}} \int d^d x \varphi_{\alpha}^*(\vec{x}, \sigma) \hat{t}_{\sigma\tau}(\vec{\nabla}) \varphi_{\alpha}(\vec{x}, \tau)$$

$$V = \langle \hat{V} \rangle = \sum_{\alpha}^{\text{occ}} \int d^d x \varphi_{\alpha}^*(\vec{x}, \sigma) \hat{v}_{\sigma\tau}^{\text{ext}}(\vec{x}) \varphi_{\alpha}(\vec{x}, \tau)$$

$$U = \langle \hat{U} \rangle = \frac{1}{2} \sum_{\alpha, \beta}^{\text{occ}} \int d^d x \int d^d x' \varphi_{\alpha}^*(\vec{x}, \sigma) \varphi_{\beta}^*(\vec{x}', \sigma') u_{\sigma\tau\sigma'\tau'}(\vec{x} - \vec{x}') \\ \times (\varphi_{\alpha}(\vec{x}, \tau) \varphi_{\beta}(\vec{x}', \tau') - \varphi_{\beta}(\vec{x}, \tau) \varphi_{\alpha}(\vec{x}', \tau'))$$

Now we extremize by functionally differentiating  $E[\{\varphi_{\alpha}, \varphi_{\alpha}^*\}]$  with respect to  $\varphi_{\alpha}^*(\vec{x}, \sigma)$ :

$$\frac{\delta T}{\delta \varphi_{\alpha}^*(\vec{x}, \sigma)} = \hat{t}_{\sigma\tau}(\vec{v}) \varphi_{\alpha}(\vec{x}, \tau)$$

$$\frac{\delta V}{\delta \varphi_{\alpha}^*(\vec{x}, \tau)} = \hat{v}_{\sigma\tau}^{\text{ext}}(\vec{x}) \varphi_{\alpha}(\vec{x}, \tau)$$

$$\frac{\delta U}{\delta \varphi_{\alpha}^*(\vec{x}, \sigma)} = \int d^d x' u_{\sigma\tau\sigma'\tau'}(\vec{x} - \vec{x}') \sum_{\beta}^{\text{occ}} \varphi_{\beta}^*(\vec{x}', \sigma') (\varphi_{\alpha}(\vec{x}, \tau) \varphi_{\beta}(\vec{x}', \tau') \\ - \varphi_{\beta}(\vec{x}, \tau) \varphi_{\alpha}(\vec{x}', \tau'))$$

To maintain orthonormality of the single-particle basis, though, we need Lagrange multipliers. Thus, what we really must extremize is

$$E^*[\{\varphi_{\alpha}, \varphi_{\alpha}^*\}] = E[\{\varphi_{\alpha}, \varphi_{\alpha}^*\}] - \sum_{\alpha, \beta} \Lambda_{\alpha\beta} (\langle \varphi_{\alpha} | \varphi_{\beta} \rangle - \delta_{\alpha\beta})$$

We can work in a basis where the Hermitian matrix  $\Lambda_{\alpha\beta}$  is diagonal, with eigenvalues  $\epsilon_{\alpha}$ . This results in



the Hartree-Fock equations,

$$\left\{ -\frac{\hbar^2}{2m} \delta_{\sigma\tau} \vec{\nabla}^2 + v_{\sigma\tau}^{\text{ext}}(\vec{x}) + v_{\sigma\tau}^{\text{H}}(\vec{x}) \right\} \varphi_a(\vec{x}, \tau) + \int d^d x' v_{\sigma\tau}^{\text{F}}(\vec{x}, \vec{x}') \varphi_a(\vec{x}', \tau) = \varepsilon_a \varphi_a(\vec{x}, \sigma)$$

where

$$v_{\sigma\tau}^{\text{H}}(\vec{x}) = \int d^d x' u_{\sigma\tau\sigma'\tau'}(\vec{x} - \vec{x}') \sum_b^{\text{occ}} \varphi_b^*(\vec{x}', \sigma') \varphi_b(\vec{x}', \tau')$$

$$v_{\sigma\tau}^{\text{F}}(\vec{x}, \vec{x}') = -u_{\sigma\tau\sigma'\tau'}(\vec{x} - \vec{x}') \sum_b^{\text{occ}} \varphi_b^*(\vec{x}', \sigma') \varphi_b(\vec{x}, \tau')$$

are the Hartree and Fock potentials, respectively.

Note that the Fock potential is nonlocal. The single particle Hartree-Fock energies are given by

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

If we sum these single particle energies over all the occupied states, we get

$$\sum_a^{\text{occ}} \varepsilon_a = T + V + 2U \neq E = \langle \Psi | \hat{H} | \Psi \rangle$$

Thus, the sum is not the total energy! Rather,

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

where the electron in state  $|a\rangle$  is removed to form the  $(N-1)$ -particle system.

When  $v_{\sigma\tau}^{\text{ext}}(\vec{x}) = v(\vec{x})\delta_{\sigma\tau}$  and  $u_{\sigma\tau\sigma'\tau'}(\vec{x}-\vec{x}') = u(\vec{x}-\vec{x}')\delta_{\sigma\sigma'}\delta_{\tau\tau'}$ , the spin DOF is just a spectator, and the HF single particle states are  $\varphi_j(\vec{x}) \otimes \eta_\sigma$ , where  $\eta_\sigma$  is a spinor corresponding to  $|\uparrow\rangle$  or  $|\downarrow\rangle$ . We then have

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

where

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

$$v^F(\vec{x}, \vec{x}') = -u(\vec{x}-\vec{x}') \sum_l^{\text{occ}} \varphi_l^*(\vec{x}') \varphi_l(\vec{x})$$

**Self-consistency**: Note that the HF WFs  $\varphi_a(\vec{x}, \sigma)$  determine the potentials  $v_{\sigma\tau}^H(\vec{x})$  and  $v_{\sigma\tau}^F(\vec{x}, \vec{x}')$ . One numerical approach is to start with some educated guess for the  $\{\varphi_a(\vec{x}, \sigma)\}$  and then iterate:

1. Given  $\{\varphi_a(\vec{x}, \sigma)\}$ , compute  $v_{\sigma\tau}^H(\vec{x})$  and  $v_{\sigma\tau}^F(\vec{x}, \vec{x}')$ .
2. Given  $v_{\sigma\tau}^H(\vec{x})$  and  $v_{\sigma\tau}^F(\vec{x}, \vec{x}')$ , solve the HF eqns for the WFs  $\{\varphi_a(\vec{x}, \sigma)\}$ .
3. Iterate to self-consistency.

# HF theory for atoms

In atomic physics, we have

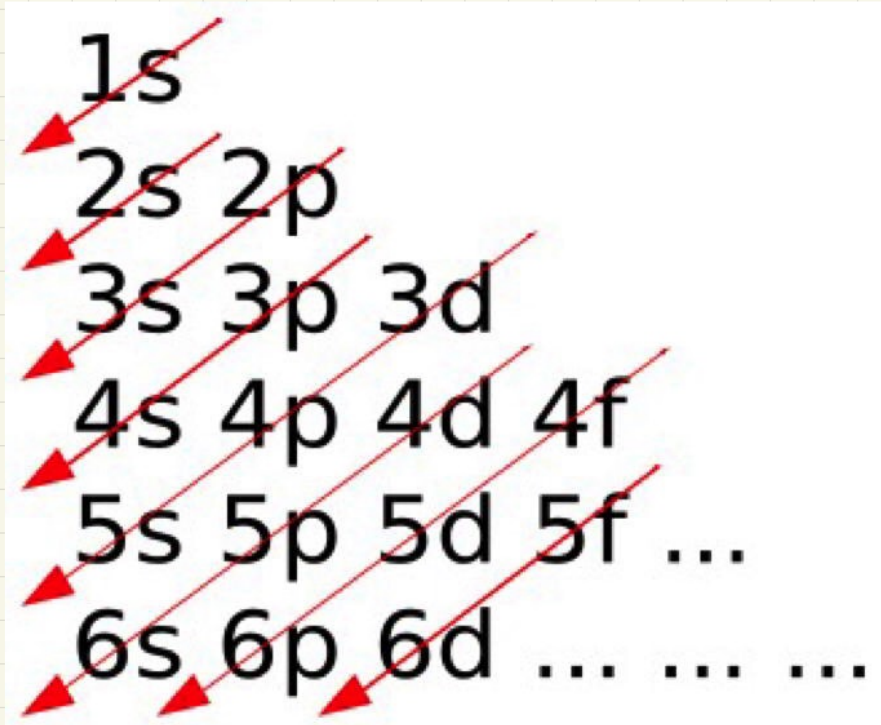
$$V^{\text{ext}}(\vec{x}) = -\frac{Ze^2}{|\vec{x}|}, \quad u(\vec{x}-\vec{x}') = \frac{e^2}{|\vec{x}-\vec{x}'|}$$

It is then a good approximation to assume that the HF wavefunctions are of the form

$$\varphi_{\alpha}(\vec{x}) = R_{nl}(r) Y_{lm}(\theta, \phi) \eta_{\sigma}$$

Thus  $\alpha = (n, l, m, \sigma)$  is a composite index, with  $n \in \{1, 2, \dots\}$ ,  $l \in \{0, 1, \dots, n-1\}$ ,  $m \in \{-l, \dots, +l\}$ , and  $\sigma \in \{-1, +1\}$ . The essential physics introduced by the HF method is that of **screening**: close to  $r=0$ , a given electron feels a nuclear potential  $-Ze^2/r$  which is unscreened. But farther away, the attractive nucleus is partially screened by the other electrons, and the potential decays faster than  $1/r$  in the  $r \rightarrow \infty$  limit. (Within Thomas-Fermi theory,  $V^{\text{scr}}(r) = -Ce^2 a_B^3 / r^4$  with  $C \approx 100$  independent of  $Z$ .) For hydrogenic atoms, the energy only depends on the principal quantum number  $n$ , and not on  $l$ . But within HF theory, smaller  $l$  means lower energy, since these states are localized nearer the nucleus, where the ionic potential is less screened. Thus, for a given  $n$ , the smaller  $l$  states fill up first. For fixed  $n$  and  $l$ ,

there are  $(2s+1) \times (2l+1) = 4l+2$  degenerate states labeled by  $m$  and  $\sigma$ ; this group of orbitals is called a **shell**.  
Filling lower  $n+l$  states first in the periodic table is



Filled shell atoms:

1s	<sup>2</sup> He	5s	<sup>38</sup> Sr
2s	<sup>4</sup> Be	4d	<sup>48</sup> Cd
2p	<sup>10</sup> Ne	5p	<sup>54</sup> Xe
3s	<sup>12</sup> Mg	6s	<sup>56</sup> Ba
3p	<sup>18</sup> Ar	4f	<sup>70</sup> Yb
4s	<sup>20</sup> Ca	5d	<sup>80</sup> Hg
3d	<sup>30</sup> Zn	6p	<sup>86</sup> Rn
4p	<sup>36</sup> Kr	7s	<sup>88</sup> Ra
		5f/6d	<sup>102</sup> No

known as the **Aufbau principle** (Aufbau (Ger.) = "construction").

## HF theory of the electron gas

The **jellium model** of the electron gas describes  $N$  electrons moving in a uniform neutralizing smeared ionic background. Since the system is translationally invariant, the HF single particle states must be plane waves:  $\varphi_{\vec{k}}(\vec{x}) = V^{-1/2} e^{i\vec{k}\cdot\vec{x}}$ .

The HF energies are

$$\varepsilon(\vec{k}) = \frac{\hbar^2 \vec{k}^2}{2m} - \int \frac{d^3 k'}{(2\pi)^3} \frac{4\pi e^2}{|\vec{k}-\vec{k}'|^2} \Theta(k_F - k') \equiv \varepsilon_0(\vec{k}) + \Sigma(\vec{k})$$

$\hbar^2 \vec{k}^2 / 2m$   
 $\downarrow$   
 "self-energy"

$\swarrow$   
 Hartree term cancelled by neutralizing background

The electron self-energy is computed to be

$$\Sigma(\mathbf{k}) = \frac{e^2 k_F}{2\pi} \left( \frac{k^2 - k_F^2}{k k_F} \ln \left| \frac{k + k_F}{k - k_F} \right| - 2 \right)$$

Expanding about  $k = k_F$ , we write  $\mathbf{k} = (k_F + q) \hat{n}$ , whence

$$\varepsilon(k_F + q) = \varepsilon_F + \frac{\hbar^2 k_F}{m} q + \frac{e^2}{\pi} q \ln \left| \frac{2k_F}{q} \right| + \mathcal{O}(q^2)$$

where  $\varepsilon_F = \frac{\hbar^2 k_F^2}{2m} - \frac{e^2 k_F}{\pi}$  is the Fermi energy within

HF theory. The velocity in the vicinity of  $k_F$  is

$$v(q) = \frac{1}{\hbar} \frac{\partial \varepsilon(k_F + q)}{\partial q} = \frac{\hbar k_F}{m} + \frac{e^2}{\pi \hbar} \left( \ln \left| \frac{2k_F}{q} \right| - 1 \right)$$

which is logarithmically divergent as  $q \rightarrow 0$ . The reason for this is that the HF many-body WF does not incorporate electron screening. More on this later! The total kinetic energy per particle is

$$\frac{T}{N} = \frac{1}{N} \times 2 \sum_{|\mathbf{k}| < k_F} \varepsilon_0(\mathbf{k}) = \frac{2}{n} \int \frac{d^3 k}{(2\pi)^3} \frac{\hbar^2 k^2}{2m} \Theta(k_F - k) = \frac{3\hbar^2 k_F^2}{10m}$$

The total potential energy comes from four contributions:

(i) self-interaction of the neutralizing background, (ii) the interaction energy of the neutralizing background with the electron gas, (iii) the Hartree energy of the electron gas,

and (iv) the exchange (Fock) energy of the electron gas. The first three terms sum to zero, leaving

$$\frac{E_x}{N} = \frac{1}{2N} \times 2 \sum_{\substack{\mathbf{k} \\ |\mathbf{k}| < k_F}} \sum (\frac{\hbar}{k}) = \frac{1}{n} \int \frac{d^3k}{(2\pi)^3} \sum (\frac{\hbar}{k}) \Theta(k_F - k) = -\frac{3e^2 k_F}{4\pi}$$

It's convenient to define the dimensionless length  $r_s$  by

$$\frac{4}{3} \pi (r_s a_B)^3 n = 1$$

where  $a_B = \hbar^2 / me^2 = 0.529 \text{ \AA}$  is the Bohr radius. Note

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

Then we have

$$\frac{T}{N} = \frac{3}{5} \left(\frac{9\pi}{4}\right)^{2/3} \frac{e^2}{2a_B} \cdot \frac{1}{r_s^2} \approx \frac{2.21}{r_s^2} \text{ Ryd}$$

$$\frac{E_x}{N} = -\frac{3}{2\pi} \left(\frac{9\pi}{4}\right)^{1/3} \frac{e^2}{2a_B} \cdot \frac{1}{r_s} \approx -\frac{0.916}{r_s} \text{ Ryd}$$

We see that interaction contributions to the total energy dominate when  $r_s$  is small, where the density  $n$  is large. This is because the kinetic energy term involves two gradients, scaling as  $L^{-2}$ , while the Coulomb interaction scales as  $L^{-1}$ . Short-ranged interactions dominate at large densities.