Hartree-Fock

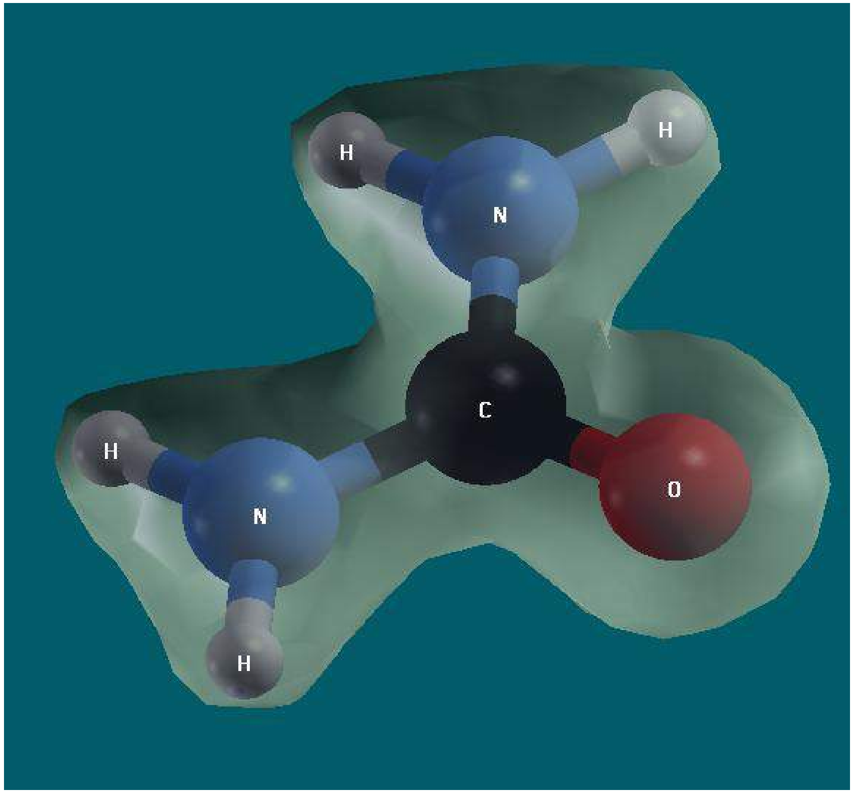
Adiabatic approximation

Independent electrons in an effective potential

Hartree–Fock

Density Functional Theory

MBPT - GW



Hartree-Fock

Douglas

Vladimir Aleksandrovich

Quantum Mechanics of the Electronic Problem

$$\mathcal{H}_{el}(\mathbf{R})\Phi_\nu(\mathbf{r}|\mathbf{R}) = E_\nu(\mathbf{R})\Phi_\nu(\mathbf{r}|\mathbf{R})$$

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{Nel}\frac{p_i^2}{2m_e} + \sum_{i=1}^{Nel}\underbrace{\sum_{I=1}^{Nat}\frac{-Z_I e^2}{|r_i - R_I|}}_{v(r_i|\mathbf{R})} + \frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}^{Nel}\underbrace{\frac{e^2}{|r_i - r_j|}}_{w(r_i - r_j)} + \underbrace{\frac{1}{2}\sum_{\substack{I,J\\ I\neq J}}^{Nat}\frac{Z_I Z_J e^2}{|R_I - R_J|}}_{E_{ion}(\mathbf{R})}$$

Quantum Mechanics of the Electronic Problem

$$\mathcal{H}_{el}\ \Phi_\nu(\mathbf{r}) = E_\nu\ \Phi_\nu(\mathbf{r})$$

$$\mathcal{H}_{el}(\mathbf{R}) = \underbrace{\sum_{i=1}^{Nel}\frac{p_i^2}{2m_e} + \sum_{i=1}^{Nel}\underbrace{\sum_{I=1}^{Nat}\frac{-Z_I e^2}{|r_i - R_I|}}_{v(r_i)}}_{\text{single particle operator}} + \underbrace{\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}^{Nel}\underbrace{\frac{e^2}{|r_i - r_j|}}_{w(r_i - r_j)}}_{\substack{\text{e-e interaction}\\ \text{2-particle op.}}} + \frac{1}{2}\underset{\text{constant}}{\underbrace{\sum_{\substack{I,J\\ I\neq J}}^{Nat}\frac{Z_I Z_J e^2}{|R_I - R_J|}}_{E_{ion}}}$$

Variational formulation of Quantum Mechanics

given $\mathcal{H}\,\Phi = E\,\Phi$

define $\mathcal{F}[\Phi] = \dfrac{\langle\Phi|\mathcal{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle}$ on the physically acceptable wavefunctions of N electrons

1) $\Phi(\mathbf{r})$ is an eigenstate of the problem with eigenvalue E

2) $\Phi(\mathbf{r})$ makes stationary the functional $\mathcal{F}$ with $E = \mathcal{F}[\Phi]$

1) and 2) are equivalent

Variational formulation of Quantum Mechanics

1) => 2)

$$\mathcal{H}\,\Phi_\nu = E_\nu\,\Phi_\nu, \quad \text{with} \quad \langle \Phi_\mu | \Phi_\nu \rangle = \delta_{\mu\nu}$$

$$\Phi_\nu \rightarrow \Phi_\nu + \delta\Phi_\nu = (1+\gamma)(\Phi_\nu + \Delta\Phi_\nu), \quad \text{with} \quad \langle \Delta\Phi_\nu | \Phi_\nu \rangle = 0$$

$$\begin{aligned}\mathcal{F}[\Phi_\nu + \delta\Phi_\nu] &= \frac{\langle \Phi_\nu + \Delta\Phi_\nu | \mathcal{H} | \Phi_\nu + \Delta\Phi_\nu \rangle}{\langle \Phi_\nu + \Delta\Phi_\nu | \Phi_\nu + \Delta\Phi_\nu \rangle} \\ &= \frac{E_\nu + \cancel{\langle \Delta\Phi_\nu | \mathcal{H} | \Phi_\nu \rangle} + c.c. + \mathcal{O}(|\Delta\Phi_\nu|^2)}{1 + \cancel{\langle \Delta\Phi_\nu | \Phi_\nu \rangle} + c.c. + \mathcal{O}(|\Delta\Phi_\nu|^2)} \\ &= E_\nu + \mathcal{O}(|\Delta\Phi_\nu|^2)\end{aligned}$$

hence

$$\delta\mathcal{F}[\Phi_\nu] = 0, \quad \text{with} \quad \mathcal{F}[\Phi_\nu] = E_\nu$$

Variational formulation of Quantum Mechanics

Similarly it can be shown that 2) => 1)

in particular it can be shown that ….

Variational Principle of Quantum Mechanics

$$\mathcal{F}[\Phi] = \frac{\langle\Phi|\mathcal{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle}$$

is stationary on the eigenstates of the QM problem and has **its only minimum** when Φ is the **Ground State**

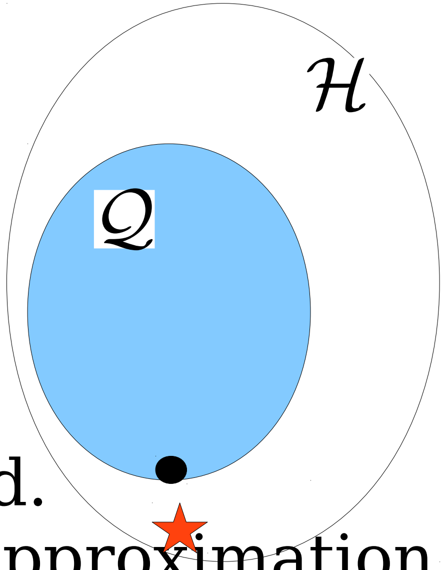
$$\Phi = \sum_\nu c_\nu \Phi_\nu, \quad \text{with} \quad \mathcal{H}\Phi_\nu = E_\nu \Phi_\nu, \quad E_0 < E_1 < E_2 < \ldots$$

$$\mathcal{F}[\Phi] = \frac{\sum_\nu |c_\nu|^2 E_\nu}{\sum_\nu |c_\nu|^2} = E_0 + \underbrace{\frac{\sum_\nu |c_\nu|^2 (E_\nu - E_0)}{\sum_\nu |c_\nu|^2}}_{>0 \text{ unless } c_\nu = 0 \quad \forall \nu \neq 0}$$

Variational Method to Approximate the GS of Quantum Mechanical Systems

Seek the minimum of $\mathcal{F}[\Phi] = \dfrac{\langle\Phi|\mathcal{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle}$ on a set $\mathcal{Q}$ of *physically acceptable* trial wavefunctions.

The wavefunction corresponding to the minimum in $\mathcal{Q}$
is the variational best solution and the value of $\mathcal{F}[\Phi_{min}]$
is the corresponding variational GS energy



$$\min_{\Phi\in\mathcal{Q}} \frac{\langle\Phi|\mathcal{H}|\Phi\rangle}{\langle\Phi|\Phi\rangle} \geq E_0$$

If $\Phi_0 \in \mathcal{Q}$ the exact solution can be obtained.
usually it is not the case and Φ_{min} is an approximation

Back to the Electronic Problem

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m_e}+v(r_i)\right)+\frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}^{N}\frac{e^2}{|r_i-r_j|}+\cancel{E_{ion}}$$

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{N} h(r_i,p_i) \ + \ \frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}^{N} w(r_i,r_j)$$

Electrons are all alike and the Hamiltonian is invariant w.r.t. permutations of the particles

The *mathematical* Hilbert space of N particles can be decomposed in *invariant subspaces* under the group of particle permutations.

Back to the Electronic Problem

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m_e} + v(r_i)\right) + \frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}^{N}\frac{e^2}{|r_i - r_j|} + \cancel{E_{ion}}$$

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{N} h(r_i, p_i) \; + \; \frac{1}{2}\sum_{\substack{i,j\\ i\neq j}}^{N} w(r_i, r_j)$$

Electrons are all alike and the Hamiltonian is invariant w.r.t. permutations of the particles

The *mathematical* Hilbert space of N particles can be decomposed in a fermionic subspace, a bosonic one and a reminder.

$$\mathcal{H}_N = \mathcal{F}_N \oplus \mathcal{B}_N \oplus \mathcal{R}_N \quad \left\{ \begin{array}{l} \mathcal{F}_N : \text{ antisymm. wfcs.} \\ \mathcal{B}_N : \text{ symm. wfcs.} \end{array} \right.$$

Back to the Electronic Problem

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{N}\left(\frac{p_i^2}{2m_e} + v(r_i)\right) + \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}}^{N}\frac{e^2}{|r_i - r_j|} + \cancel{E_{ion}}$$

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{N} h(r_i, p_i) \; + \; \frac{1}{2}\sum_{\substack{i,j \\ i\neq j}}^{N} w(r_i, r_j)$$

Electrons are **fermions** => totally antisymmetric wfcs.

only wfcs in $\mathcal{F}_N$ are physically acceptable

for any $\mathcal{P}(1, 2, ..., N) \longrightarrow (p_1, p_2, ..., p_N)$

$$\mathcal{P}\Phi(r_1, r_2, ..., r_N) \longrightarrow \Phi(r_{p_1}, r_{p_2}, ..., r_{p_N}) = (-)^{\varepsilon(\mathcal{P})}\Phi(r_1, r_2, ..., r_N)$$

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- ma per seguir virtute e conoscenza -

The Antisymmetrizer

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_{\mathcal{P}}^{N!} (-)^{\varepsilon(\mathcal{P})} \mathcal{P}, \qquad \mathcal{S} = \frac{1}{\sqrt{N!}} \sum_{\mathcal{P}}^{N!} \mathcal{P}$$

$$[\mathcal{A}, \mathcal{H}_{el}] = 0, \qquad [\mathcal{S}, \mathcal{H}_{el}] = 0$$

P is a projector *iff* $P = P^\dagger,\ P^2 = P \ \Rightarrow\ P\psi = \alpha\psi,\ \alpha = 0, 1$

P projects on the subspace of $\alpha = 1$

$\frac{1}{\sqrt{N!}}\mathcal{A}$ projects on $\mathcal{F}_N$, $\frac{1}{\sqrt{N!}}\mathcal{S}$ projects on $\mathcal{B}_N$

$$\mathcal{A}^2 = \sqrt{N!}\mathcal{A}, \quad \mathcal{A} = \mathcal{A}^\dagger$$

Stater determinants

N-particle product wavefunctions (Hartree products)

$$\Phi^{\{H\}}(\mathbf{r}) = \phi_1(r_1)\phi_2(r_2)...\phi_N(r_N)$$

can form a basis for the *mathematical* Hilbert space, but ...

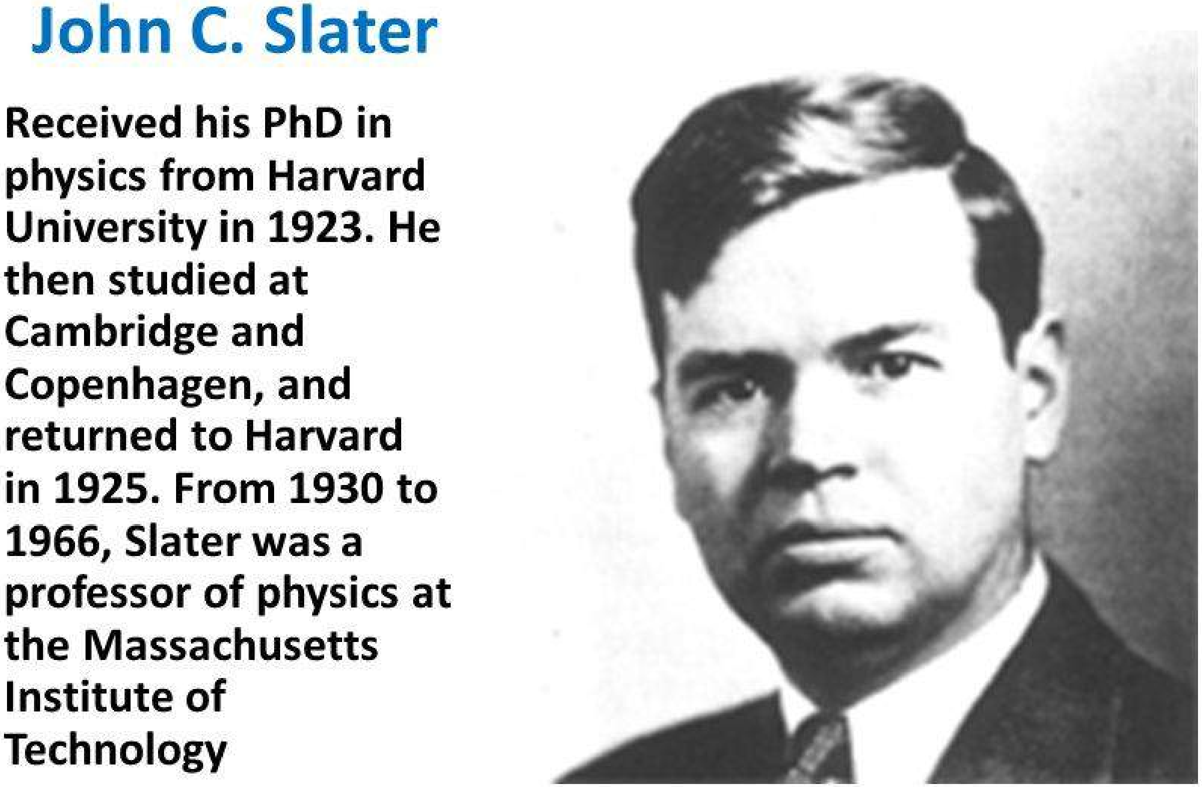
Stater determinants

N-particle product wavefunctions (Hartree products)

$$\Phi^{\{H\}}(\mathbf{r}) = \phi_1(r_1)\phi_2(r_2)...\phi_N(r_N)$$

do not belong to the Fermionic subspace;

enters



John C. Slater

Received his PhD in physics from Harvard University in 1923. He then studied at Cambridge and Copenhagen, and returned to Harvard in 1925. From 1930 to 1966, Slater was a professor of physics at the Massachusetts Institute of Technology

Stater determinants

N-particle product wavefunctions (Hartree products)

$$\Phi^{\{H\}}(\mathbf{r}) = \phi_1(r_1)\phi_2(r_2)...\phi_N(r_N)$$

do not belong to the Fermionic subspace; **are not acceptable**

$$\Phi^{\{S\}}(\mathbf{r}) = \mathcal{A}\Phi^{\{H\}}(\mathbf{r}) = \frac{1}{\sqrt{N!}}\sum_{\mathcal{P}}(-)^{\varepsilon(\mathcal{P})}\phi_1(r_{p_1})\phi_2(r_{p_2})...\phi_N(r_{p_N})$$

$$= \frac{1}{\sqrt{N!}}\sum_{\mathcal{P}}(-)^{\varepsilon(\mathcal{P})}\phi_{p_1}(r_1)\phi_{p_2}(r_2)...\phi_{p_N}(r_N)$$

Slater determinants are acceptable Fermionic wfcs

$$= \frac{1}{\sqrt{N!}}\begin{vmatrix} \phi_1(r_1) & \phi_2(r_1) & \cdots & \phi_N(r_1) \\ \phi_1(r_2) & \phi_2(r_2) & \cdots & \phi_N(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_1(r_N) & \phi_2(r_N) & \cdots & \phi_N(r_N) \end{vmatrix}$$

can form a basis for $\mathcal{F}_N$

Hartree-Fock Variational Approximation

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{N} h(r_i, p_i) \; + \; \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}}^{N} w(r_i, r_j)$$

seek the variational minimum of the energy expection value among Fermionic wfcs given by a **single Slater determinant**

$$E^{HF} = \min_{\Phi^{\{S\}} = \mathcal{A}[\phi_1 \cdots \phi_N]} \frac{\langle \Phi^{\{S\}} | \mathcal{H}_{el} | \Phi^{\{S\}} \rangle}{\langle \Phi^{\{S\}} | \Phi^{\{S\}} \rangle}$$

The variational parameters are the single particle orbitals

NB: the variational space is not a subspace

Slater Determinant Normalization

The Slater determinant is normalized if the single-particle orbitals are orthonormal (not a loss of generality)

$$\langle \Phi^{\{S\}} | \Phi^{\{S\}} \rangle = \langle \Phi^{\{H\}} | A^\dagger A | \Phi^{\{H\}} \rangle = \langle \Phi^{\{H\}} | A^2 | \Phi^{\{H\}} \rangle$$

$$= \sqrt{N!} \langle \Phi^{\{H\}} | A | \Phi^{\{H\}} \rangle$$

$$= \sum_{\mathcal{P}} (-)^{\varepsilon(\mathcal{P})} \int [\, \phi_1^*(r_1)\ \phi_2^*(r_2) \cdots \phi_N^* | (r_N)\ ] \times$$
$$[\phi_{p_1}(r_1) \phi_{p_2}(r_2) \cdots \phi_{p_N}(r_N)]\, dr_1 dr_2 \cdots dr_N$$

$$= \sum_{\mathcal{P}} (-)^{\varepsilon(\mathcal{P})} \langle \phi_1 | \phi_{p_1} \rangle \langle \phi_2 | \phi_{p_2} \rangle \cdots \langle \phi_N | \phi_{p_N} \rangle$$

$$= \sum_{\mathcal{P}} (-)^{\varepsilon(\mathcal{P})} \delta_{1,p_1} \delta_{2,p_2} \cdots \delta_{N,p_N} \quad = \ 1$$

Slater Determinant Expectation Values

For **single particle operators** : $\mathcal{O}^{(1)} = \sum_{k=1}^{N} o^{(1)}(r_k)$

$$\langle \Phi^{\{S\}} | O^{(1)} | \Phi^{\{S\}} \rangle = \langle \Phi^{\{H\}} | A^{\dagger} O^{(1)} A | \Phi^{\{H\}} \rangle = \langle \Phi^{\{H\}} | O^{(1)} A^2 | \Phi^{\{H\}} \rangle$$

$$= \sqrt{N!} \langle \Phi^{\{H\}} | O^{(1)} A | \Phi^{\{H\}} \rangle$$

$$= \sum_{\mathcal{P}} (-)^{\varepsilon(\mathcal{P})} \int [\, \phi_1^*(r_1)\ \phi_2^*(r_2) \cdots \phi_N^* |(r_N)\,] \left(\sum_{k=1}^{N} o^{(1)}(r_k) \right) \times$$

$$[\phi_{p_1}(r_1) \phi_{p_2}(r_2) \cdots \phi_{p_N}(r_N)]\ dr_1 dr_2 \cdots dr_N$$

$$= \sum_{k=1}^{N} \sum_{\mathcal{P}}^{N!} (-)^{\varepsilon(\mathcal{P})} \langle \phi_1 | \phi_{p_1} \rangle \langle \phi_2 | \phi_{p_2} \rangle \cdots \langle \phi_k | o^{(1)} | \phi_{p_k} \rangle \cdots \langle \phi_N | \phi_{p_N} \rangle$$

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$$= \sqrt{N!} \langle \Phi^{\{H\}} | O^{(1)} A | \Phi^{\{H\}} \rangle$$

$$= \sum_{\mathcal{P}} (-)^{\varepsilon(\mathcal{P})} \int [\, \phi_1^*(r_1)\, \phi_2^*(r_2) \cdots \phi_N^* | (r_N)\,] \left(\sum_{k=1}^{N} o^{(1)}(r_k) \right) \times$$

$$[\phi_{p_1}(r_1) \phi_{p_2}(r_2) \cdots \phi_{p_N}(r_N)]\; dr_1 dr_2 \cdots dr_N$$

$$= \sum_{k=1}^{N} \sum_{\mathcal{P}}^{N!} (-)^{\varepsilon(\mathcal{P})} \delta_{1,p_1} \delta_{2,p_2} \cdots \langle \phi_k | o^{(1)} | \phi_{p_k} \rangle \cdots \delta_{N,p_N}$$

$$\mathcal{P} : \qquad p_1 \to 1, p_2 \to 2, \cdots, p_k \to ?, \cdots, p_N \to N$$

$$p_k \to k$$

Slater Determinant Expectation Values

For **single particle operators** : $\mathcal{O}^{(1)} = \sum_{k=1}^{N} o^{(1)}(r_k)$

$$\langle\Phi^{\{S\}}|O^{(1)}|\Phi^{\{S\}}\rangle = \langle\Phi^{\{H\}}|A^{\dagger}O^{(1)}A|\Phi^{\{H\}}\rangle = \langle\Phi^{\{H\}}|O^{(1)}A^{2}|\Phi^{\{H\}}\rangle$$

$$= \sqrt{N!}\langle\Phi^{\{H\}}|O^{(1)}A|\Phi^{\{H\}}\rangle$$

$$= \sum_{\mathcal{P}}(-)^{\varepsilon(\mathcal{P})}\int[\ \phi_1^*(r_1)\ \phi_2^*(r_2)\cdots\phi_N^*|(r_N)\ ]\left(\sum_{k=1}^{N} o^{(1)}(r_k)\right)\times$$
$$[\phi_{p_1}(r_1)\phi_{p_2}(r_2)\cdots\phi_{p_N}(r_N)]\ dr_1 dr_2\cdots dr_N$$

$$= \sum_{k=1}^{N}\sum_{\mathcal{P}}^{N!}(-)^{\varepsilon(\mathcal{P})}\delta_{1,p_1}\delta_{2,p_2}\cdots\langle\phi_k|o^{(1)}|\phi_{p_k}\rangle\cdots\delta_{N,p_N}$$

$$= \sum_{k=1}^{N}\langle\phi_k|o^{(1)}|\phi_k\rangle$$

Slater Determinant Expectation Values

For **single particle operators** : $\mathcal{O}^{(1)} = \sum_{k=1}^{N} o^{(1)}(r_k)$

$$\langle \Phi^{\{S\}} | O^{(1)} | \Phi^{\{S\}} \rangle = \sum_{k=1}^{N} \langle \phi_k | o^{(1)} | \phi_k \rangle$$

$$\langle \Phi^{\{S\}} | n(r) | \Phi^{\{S\}} \rangle = \sum_{k=1}^{N} \langle \phi_k | \delta(r_k - r) | \phi_k \rangle = \sum_{k=1}^{N} |\phi_k(r)|^2$$

$$\langle \Phi^{\{S\}} | V_{ext} | \Phi^{\{S\}} \rangle = \sum_{k=1}^{N} \int v_{ext}(r) |\phi_k(r)|^2 dr = \int v_{ext}(r) n(r) dr$$

$$\langle \Phi^{\{S\}} | T_e | \Phi^{\{S\}} \rangle = \sum_{k=1}^{N} \langle \phi_k | \frac{p^2}{2m} | \phi_k \rangle = \sum_{k=1}^{N} \langle \phi_k | -\frac{\hbar^2}{2m} \nabla^2 | \phi_k \rangle$$

Slater Determinant Expectation Values

For **2-particle operators** : $\mathcal{O}^{(2)} = \frac{1}{2}\sum_{i\neq j}^{N} o^{(2)}(r_i, r_j)$

$$\langle\Phi^{\{S\}}|O^{(2)}|\Phi^{\{S\}}\rangle = \langle\Phi^{\{H\}}|A^{\dagger}O^{(2)}A|\Phi^{\{H\}}\rangle = \langle\Phi^{\{H\}}|O^{(2)}A^{2}|\Phi^{\{H\}}\rangle$$

$$= \sqrt{N!}\langle\Phi^{\{H\}}|O^{(2)}A|\Phi^{\{H\}}\rangle$$

$$= \sum_{\mathcal{P}}(-)^{\varepsilon(\mathcal{P})}\int[\,\phi_1^*(r_1)\;\phi_2^*(r_2)\cdots\phi_N^*|(r_N)\,]\left(\frac{1}{2}\sum_{i\neq j}^{N}o^{(2)}(r_i,r_j)\right)$$

$$[\phi_{p_1}(r_1)\phi_{p_2}(r_2)\cdots\phi_{p_N}(r_N)]\;dr_1 dr_2\cdots dr_N$$

$$= \frac{1}{2}\sum_{i\neq j}^{N}\sum_{\mathcal{P}}^{N!}(-)^{\varepsilon(\mathcal{P})}\delta_{1,p_1}\delta_{2,p_2}\cdots\langle\underbrace{\phi_i\overbrace{\phi_j|o^{(2)}|\phi_{p_i}}^{}}_{}\phi_{p_j}\rangle\cdots\delta_{N,p_N}$$

$$\mathcal{P}:\quad p_1\to 1, p_2\to 2,\cdots,p_i\to ?,\cdots,p_j\to ?,\cdots p_N\to N$$

$$p_i\to i \qquad p_j\to j \qquad (-)^{\varepsilon(\mathcal{P})} = +1$$

$$p_i\to j \qquad p_j\to i \qquad (-)^{\varepsilon(\mathcal{P})} = -1$$

Slater Determinant Expectation Values

For **2-particle operators** : $\mathcal{O}^{(2)} = \dfrac{1}{2}\sum_{i\neq j}^{N} o^{(2)}(r_i, r_j)$

$$\langle\Phi^{\{S\}}|O^{(2)}|\Phi^{\{S\}}\rangle = \langle\Phi^{\{H\}}|A^{\dagger}O^{(2)}A|\Phi^{\{H\}}\rangle = \langle\Phi^{\{H\}}|O^{(2)}A^2|\Phi^{\{H\}}\rangle$$

$$= \sqrt{N!}\langle\Phi^{\{H\}}|O^{(2)}A|\Phi^{\{H\}}\rangle$$

$$= \sum_{\mathcal{P}}(-)^{\varepsilon(\mathcal{P})}\int[\,\phi_1^*(r_1)\;\phi_2^*(r_2)\cdots\phi_N^*|(r_N)\,]\left(\frac{1}{2}\sum_{i\neq j}^{N} o^{(2)}(r_i, r_j)\right)$$
$$[\phi_{p_1}(r_1)\phi_{p_2}(r_2)\cdots\phi_{p_N}(r_N)]\;dr_1 dr_2\cdots dr_N$$

$$= \frac{1}{2}\sum_{i\neq j}^{N}\sum_{\mathcal{P}}^{N!}(-)^{\varepsilon(\mathcal{P})}\delta_{1,p_1}\delta_{2,p_2}\cdots\langle\underbrace{\phi_i\overbrace{\phi_j|o^{(2)}|\phi_{p_i}}}\phi_{p_j}\rangle\cdots\delta_{N,p_N}$$

$$= \frac{1}{2}\sum_{i\neq j}^{N}\Big(\langle\phi_i\phi_j|o^{(2)}|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|o^{(2)}|\phi_j\phi_i\rangle\Big)$$

Slater Determinant Expectation Values

For **2-particle operators** : $\mathcal{O}^{(2)} = \frac{1}{2} \sum_{i \neq j}^{N} o^{(2)}(r_i, r_j)$

$$\langle \Phi^{\{S\}} | O^{(2)} | \Phi^{\{S\}} \rangle = \frac{1}{2} \sum_{i \neq j}^{N} \Big(\langle \phi_i \phi_j | o^{(2)} | \phi_i \phi_j \rangle - \langle \phi_i \phi_j | o^{(2)} | \phi_j \phi_i \rangle \Big)$$

Slater Determinant Expectation Values

For **2-particle operators** : $\mathcal{O}^{(2)} = \frac{1}{2}\sum_{i\neq j}^{N} o^{(2)}(r_i, r_j)$

$$\langle \Phi^{\{S\}} | O^{(2)} | \Phi^{\{S\}} \rangle = \frac{1}{2}\sum_{i,j}^{N} \Big(\langle \phi_i\phi_j | o^{(2)} | \phi_i\phi_j \rangle - \langle \phi_i\phi_j | o^{(2)} | \phi_j\phi_i \rangle \Big)$$

$$\langle \Phi^{\{S\}} | W_{ee} | \Phi^{\{S\}} \rangle = \frac{1}{2}\sum_{i,j}^{N} (\langle \underbrace{\phi_i \overbrace{\phi_j | w | \phi_i}^{}}_{} \phi_j \rangle - \langle \underbrace{\phi_i \overbrace{\phi_j | w | \phi_j}^{}}_{} \phi_i \rangle)$$

$$= \frac{1}{2}\sum_{i,j}^{N} \int |\phi_i(r)|^2 \; w(r, r') \; |\phi_j(r')|^2 \; dr dr'$$

$$-\frac{1}{2}\sum_{i,j}^{N} \int \phi_i^*(r)\phi_j(r)\, w(r, r')\, \phi_j^*(r')\phi_i(r')\, dr dr'$$

Slater Determinant Expectation Values

For **2-particle operators** : $\mathcal{O}^{(2)} = \frac{1}{2}\sum_{i\neq j}^{N} o^{(2)}(r_i, r_j)$

$$\langle\Phi^{\{S\}}|O^{(2)}|\Phi^{\{S\}}\rangle = \frac{1}{2}\sum_{i,j}^{N}\Big(\langle\phi_i\phi_j|o^{(2)}|\phi_i\phi_j\rangle - \langle\phi_i\phi_j|o^{(2)}|\phi_j\phi_i\rangle\Big)$$

$$\langle\Phi^{\{S\}}|W_{ee}|\Phi^{\{S\}}\rangle = \frac{1}{2}\sum_{i,j}^{N}\big(\langle\underbrace{\phi_i\overbrace{\phi_j|w|\phi_i}^{}}_{}\phi_j\rangle - \langle\underbrace{\phi_i\overbrace{\phi_j|w|\phi_j}^{}}_{}\phi_i\rangle\big)$$

$$= \frac{1}{2}\int n(r)w(r,r')n(r') - \frac{1}{2}\int|\gamma(r,r')|^2 w(r,r')$$

$$n(r) = \sum_k |\phi_k(r)|^2, \qquad \gamma(r,r') = \sum_k \phi_k(r)\phi_k^*(r')$$

Density and 1-particle Density Matrix of $\Phi^{\{S\}}$

Hartree-Fock Energy Functional

$$E^{HF}[\Phi^{\{S\}}] = \sum_i \langle\phi_i| - \frac{\hbar^2}{2m}\nabla^2|\phi_i\rangle + \int v_{ext}(r)n(r)\,dr$$

Hartree energy
E$_H$ > 0

$$+\frac{1}{2}\sum_{i,j}^{N}\int |\phi_i(r)|^2\ \frac{e^2}{|r-r'|}\ |\phi_j(r')|^2\ dr dr'$$

Exchange (Fock) energy
E$_x$ < 0

$$-\frac{1}{2}\sum_{i,j}^{N}\int \phi_i^*(r)\phi_j(r)\ \frac{e^2}{|r-r'|}\ \phi_j^*(r')\phi_i(r')\,dr dr'$$

orthogonality conditions

$$-\sum_{i,j}^{N}\Lambda_{i,j}\left(\langle\phi_i|\phi_j\rangle - \delta_{ij}\right)$$

$\delta\ E^{HF}[\Phi^{\{S\}}] = 0$ leads to the **Hartree-Fock eqs**

Hartree-Fock equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(r) + \sum_j^N \int |\phi_j(r')|^2 \frac{e^2}{|r-r'|}dr'\right]\phi_i(r)$$

$$-\sum_j^N \int \phi_j(r)\frac{e^2}{|r-r'|}\phi_j^*(r')\phi_i(r')dr' = \sum_j \Lambda_{i,j}\phi_j(r)$$

Hartree-Fock equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(r) + e^2\int \frac{n(r')}{|r-r'|}dr'\right]\phi_i(r)$$

$$-\sum_j^N \int \phi_j(r)\frac{e^2}{|r-r'|}\phi_j^*(r')\phi_i(r')dr' = \sum_j \Lambda_{i,j}\phi_j(r)$$

Hartree-Fock equations

$$
\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(r) + e^2 \int \frac{n(r')}{|r-r'|}dr'\right]\phi_i(r)
$$

$$
- e^2 \int \frac{\gamma(r,r')}{|r-r'|}\phi_i(r')dr' = \sum_j \Lambda_{i,j}\phi_j(r)
$$

Hartree-Fock equations

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(r) + e^2\int \frac{n(r')}{|r-r'|}dr'\right]\phi_i(r)$$

$$- e^2\int \frac{\gamma(r,r')}{|r-r'|}\phi_i(r')dr' = \varepsilon_i\,\phi_i(r)$$

independent electrons in a self-consistent potential

$$V_{scf}(r) = V_{ext}(r) + e^2\int \frac{n(r')}{|r-r'|}dr' + \hat{V}_x$$

non-local exchange (Fock) operator

Douglas Hartree and Phyllis Nicolson attending the operation of the Differential Analyzer

Hartree-Fock Energy

$$E_{GS}^{HF} = \min_{\Phi^{\{S\}}} E^{HF}(\Phi^{\{S\}}) \;\geq\; E_{GS}$$

$$E_{GS} = E_{GS}^{HF} + E_{corr}, \qquad E_{corr} \leq 0$$

Chemist definition of correlation: whatever is beyond HF

Probability to find one particle in r (and one in r')

$$\langle \Phi^{\{H\}} | \delta(r_1 - r) | \Phi^{\{H\}} \rangle = |\phi_1(r)|^2$$

$$\langle \Phi^{\{H\}} | \delta(r_1 - r)\delta(r_2 - r') | \Phi^{\{H\}} \rangle = |\phi_1(r)|^2 |\phi_2(r')|^2$$

Hartree-Fock Energy

$$E_{GS}^{HF} = \min_{\Phi^{\{S\}}} E^{HF}(\Phi^{\{S\}}) \ \geq \ E_{GS}$$

$$E_{GS} = E_{GS}^{HF} + E_{corr}, \qquad E_{corr} \leq 0$$

Chemist definition of correlation: whatever is beyond HF

Probability to find one particle in r (and one in r')

$$\langle \Phi^{\{S\}} | \delta(r_1 - r) | \Phi^{\{S\}} \rangle = n(r)/N$$

$$\langle \Phi^{\{S\}} | \delta(r_1 - r)\delta(r_2 - r') | \Phi^{\{S\}} \rangle = \frac{n(r)n(r') - |\gamma(r,r')|^2}{N(N-1)}$$

Local approximations for Vx

independent electrons in a self-consistent potential

$$V_{scf}(r) = V_{ext}(r) + e^2 \int \frac{n(r')}{|r-r'|} dr' + \hat{V}_x$$

non-local exchange (Fock) operator

$$\hat{V}_x \phi_i(r) = -\, e^2 \int \frac{\gamma(r,r')}{|r-r'|} \phi_i(r') dr'$$

local approximations:

Slater Potential

$$v_x^{SLA}(r) \;=\; \frac{1}{n(r)} \sum_i \phi_i^*(r) \hat{V}_x \phi_i(r)$$

statistical average

Slater, Phys. Rev. 81, 385 (1951); 82, 538 (1951)

Optimized Effective Potential

$$v_x^{OEP}(r) \quad : \quad \text{The best local potential in a variational sense}$$

Sharp and Horton, Phys. Rev. 90, 317 (1953)
Talman and Shadwick, Phys. Rev. A 14, 36 (1976)

Let's talk about spin

$$\phi(r) = \begin{pmatrix} \phi^{\uparrow}(r) \\ \phi^{\downarrow}(r) \end{pmatrix}$$

If the system is closed-shell single particle orbitals are doubly occupied with $\phi^{\uparrow}(r) = \phi^{\downarrow}(r)$

For open-shell systems one can consider

Restricted HF $\phi^{\uparrow}(r) = \phi^{\downarrow}(r)$

Unrestricted HF $\phi^{\uparrow}(r) \neq \phi^{\downarrow}(r)$

Let's talk about spin

$$\phi(r) = \begin{pmatrix} \phi^{\uparrow}(r) \\ \phi^{\downarrow}(r) \end{pmatrix} \quad \text{often just} \quad \begin{pmatrix} \phi^{\uparrow}(r) \\ 0 \end{pmatrix}, \text{ or } \begin{pmatrix} 0 \\ \phi^{\downarrow}(r) \end{pmatrix},$$

$$n(r) = \sum_i \langle \phi_i | \delta(\hat{r} - r) | \phi_i \rangle = \sum_i \sum_{\sigma=\uparrow,\downarrow} |\phi_i^{\sigma}(r)|^2$$

$$E_x = -\frac{1}{2} \sum_{i,j} \int \sum_{\alpha} \phi_i^{\alpha *}(r) \phi_j^{\alpha}(r) \frac{e^2}{|r - r'|} \sum_{\beta} \phi_j^{\beta *}(r') \phi_i^{\beta}(r')$$

$$E_x = -\frac{1}{2} \sum_{\sigma=\uparrow,\downarrow} \sum_{i,j} \int \phi_i^{\sigma *}(r) \phi_j^{\sigma}(r) \frac{e^2}{|r - r'|} \phi_j^{\sigma *}(r') \phi_i^{\sigma}(r')$$

Exchange interaction favours parallel spins

Symmetry

The symmetries enjoyed by the MB Hamiltonian are often used to constraint the variational freedom of the single particle orbitals.

For instance if the MB Hamiltonian is spin-independent (non-relativistic without an ext. magnetic filed) the single particle wfcs are taken to be spin eigenstates.

If the system has rotational symmetry (atoms) the single particle wfcs are taken as $\phi_{nlm\sigma}(\mathbf{r}) = f_{nl}(r)\, Y_{lm}(\hat{r})\, \chi_\sigma$

and so on ...

Symmetry Dilemma

If the MB Hamiltonian enjoys some symmetry its GS and the other eigenstates do transform according to a representation of the symmetry group.

If the GS is non degenerate (closed shell) *usually* this representation is the totally symmetric one, the HF effective Hamiltonian is also symmetric and the single particle states are symmetry-abiding.

Life is not always so simple.

Broken symmetry solutions may have a better (lover) energy than symmetry-respecting solutions.

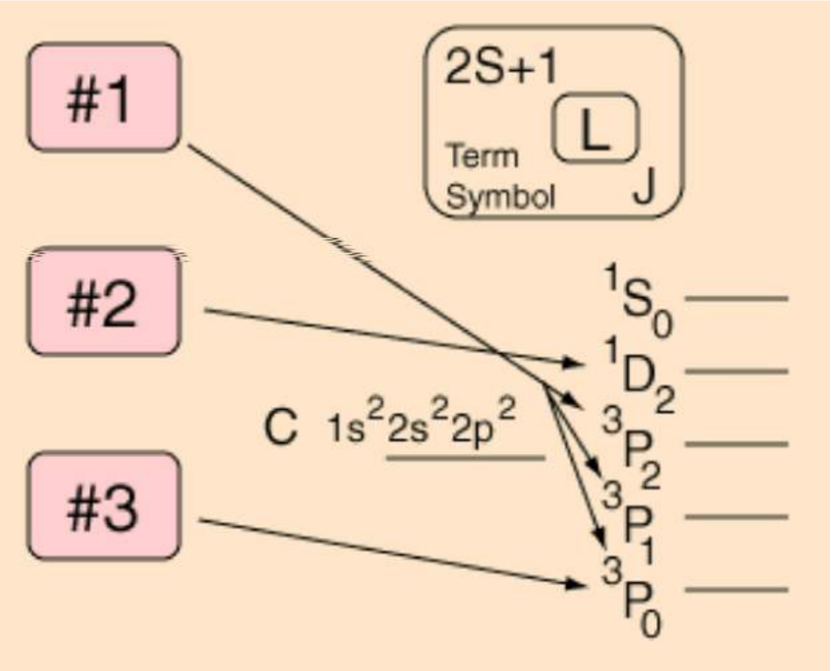
Open-shell systems are more complicated.

Hund's Rules

#1 The term with maximum multiplicty lies lowest in energy

#2 For a given multiplicity, the term with the largest value of L lies lowest in in energy.

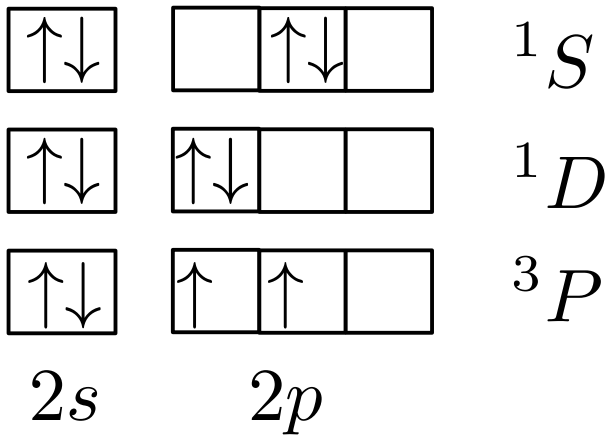
#3 For atoms with less than half-filled shells, the level with the lowest value of J lies lowest in energy.



Hund's rules assume combination to form S and L, or imply L-S (Russell-Saunders) coupling and presume that the electrons can be considered to be in a unique configuration. Neither is always true. For heavier elements, the "j-j coupling" scheme often gives better agreement with experiment.

Hund's Rules

$P^+ : \quad [He]2s^2 2p^2$



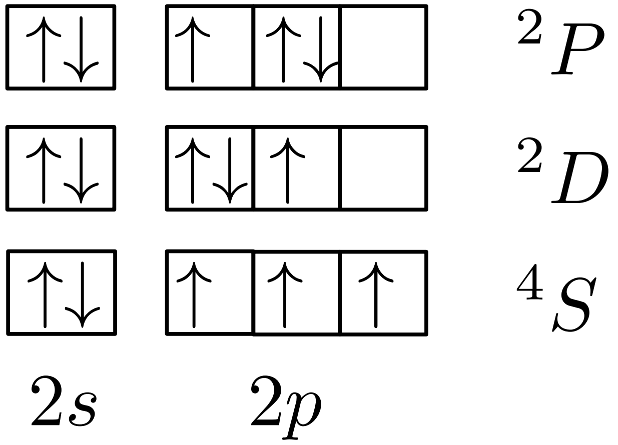
^1S

^1D

^3P

$2s \qquad 2p$

$P \quad : \quad [He]2s^2 2p^3$



^2P

^2D

^4S

$2s \qquad 2p$

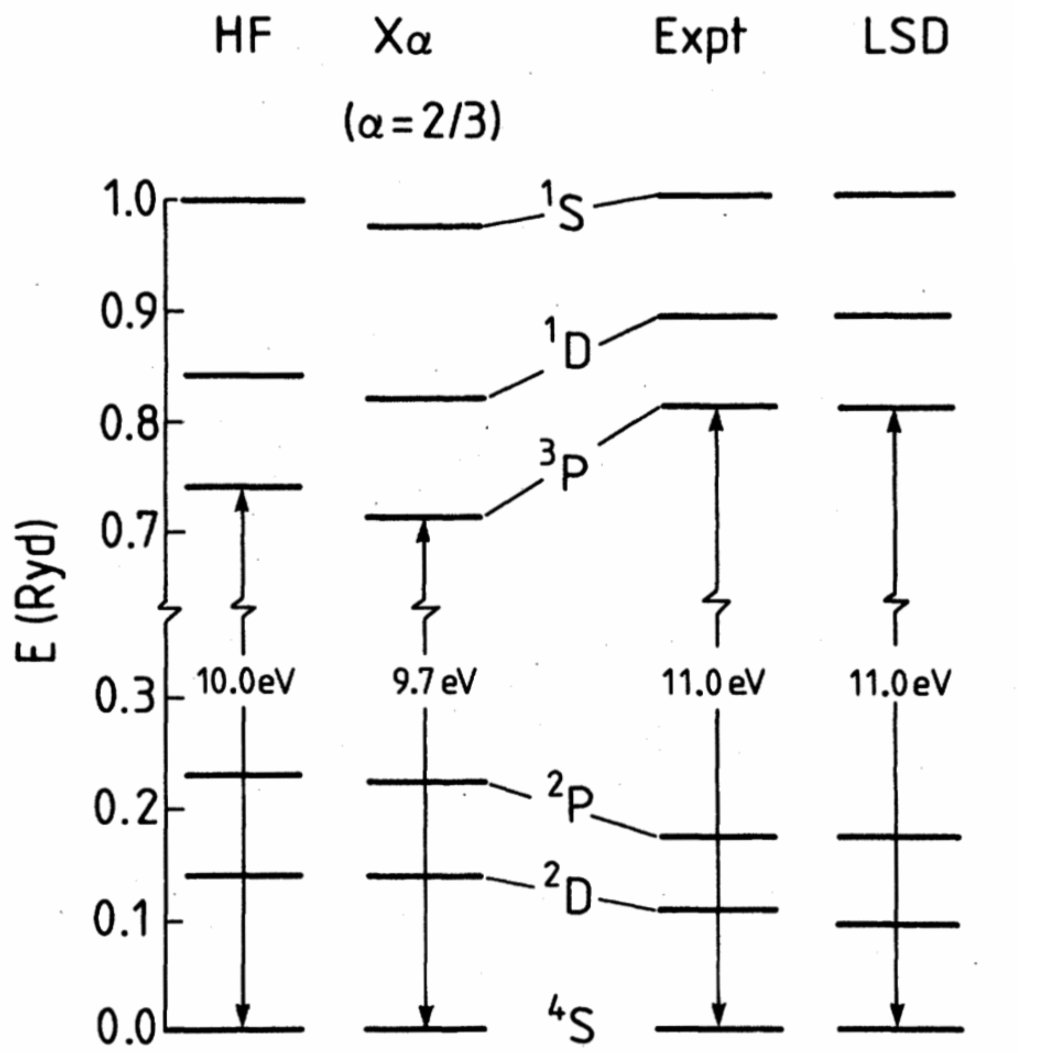


FIG. 12. Multiplet structures for P and P^+ for Hartree-Fock (HF), $X\alpha$ ($\alpha=\frac{2}{3}$), and local spin-density (LSD) calculations, compared with experiment (after Wood, 1980). The lowest levels are set to a common zero.

Wood, J. H., 1980, J. Phys. B **13**, 1.

Meaning of Hartree-Fock Eigenvalues

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + v_{ext}(r) + \sum_j^N \int |\phi_j(r')|^2 \frac{e^2}{|r-r'|} dr'\right] \phi_i(r)$$

$$-\sum_j^N |\langle\sigma_i|\sigma_j\rangle|^2 \int \phi_j(r) \frac{e^2}{|r-r'|} \phi_j^*(r')\phi_i(r') dr' = \varepsilon_i \, \phi_i(r)$$

$$h_i = \langle\phi_i| -\frac{\hbar^2}{2m}\nabla^2 + v_{ext}|\phi_i\rangle, \qquad J_{ij} = \int |\phi_i(r)|^2 \, \frac{e^2}{|r-r'|} \, |\phi_j(r')|^2,$$

$$K_{ij} = \int \phi_i^*(r)\phi_j(r) \, \frac{e^2}{|r-r'|} \, \phi_j^*(r')\phi_i(r') \, |\langle\sigma_i|\sigma_j\rangle|^2,$$

$$W_{ij} = J_{ij} - K_{ij}$$

$$\boxed{\varepsilon_i = h_i + \sum_j W_{ij}}$$

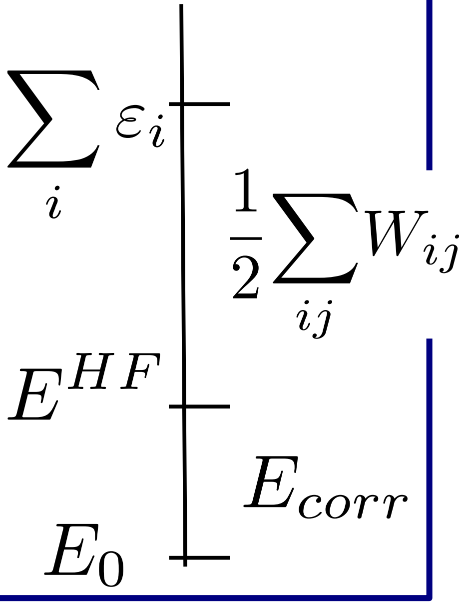
Meaning of Hartree-Fock Eigenvalues

$$\varepsilon_i = h_i + \sum_j W_{ij}$$

$$E^{HF} = \sum_i h_i + \frac{1}{2}\sum_{i,j} W_{ij} \quad \neq \sum_i \varepsilon_i$$

The HF eigenvalues are NOT single particle contribution to the total energy !

$$E^{HF} = \sum_i \varepsilon_i - \frac{1}{2}\sum_{i,j} W_{ij} \;=\; \sum_i \frac{h_i + \varepsilon_i}{2}$$



what do they represent then ?

Koopmans' First Theorem

occupied-orbital eigenvalues are approximations to *Ionization Potentials* (energy required to remove an electron)

Let $N^{(0)}$ be the GS for *N* particles : $(1\,,\,2\,,\,\ldots,i,\ldots,N)$

Let $(N-1,i)$ be the stationary state of *N-1* particles obtained removing electronic orbital *i* : $(1',2',\ldots,\cancel{i},\ldots,N')$

The *Ionization Potential* is $IP_i = E(N-1,i) - E_0(N)$

Within HF we have $IP_i \approx E^{HF}(N-1,i) - E_0^{HF}(N)$

$$E_0^{HF}(N) = \sum_k h_k + \frac{1}{2}\sum_{jk} W_{jk}$$

$$E^{HF}(N-1,i) = \sum_{k\neq i} h'_k + \frac{1}{2}\sum_{j,k\neq i} W'_{jk}$$

Koopmans': neglect orbital relaxation

Koopmans' First Theorem

occupied-orbital eigenvalues are approximations to *Ionization Potentials* (energy required to remove an electron)

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Within HF we have $IP_i \approx E^{HF}(N-1,i) - E_0^{HF}(N)$

$$E_0^{HF}(N) = \sum_k h_k + \frac{1}{2}\sum_{jk} W_{jk}$$

$$\tilde{E}^{\,K}(N-1,i) = \sum_{k\neq i} h_k + \frac{1}{2}\sum_{j,k\neq i} W_{jk}$$

Koopmans': neglect orbital relaxation

Koopmans' First Theorem

occupied-orbital eigenvalues are approximations to *Ionization Potentials* (energy required to remove an electron)

Let $N^{(0)}$ be the GS for *N* particles : $(1\,,\,2\,,\,\ldots,i,\ldots,N)$

Let $(N\!-\!1,i)$ be the stationary state of *N-1* particles obtained removing electronic orbital *i* : $(1',2',\ldots,\cancel{i},\ldots,N')$

The *Ionization Potential* is $IP_i = E(N-1,i) - E_0(N)$

Within HF we have $IP_i \approx E^{HF}(N-1,i) - E_0^{HF}(N)$

$$E_0^{HF}(N) = \sum_k h_k + \frac{1}{2}\sum_{jk} W_{jk}$$

Koopmans': neglect orbital relaxation

$$\tilde{E}^{\,K}(N-1,i) = E_0^{HF}(N) - h_i - \sum_j W_{ij}$$

$(\ W_{ii} = 0\ )$

Koopmans' First Theorem

occupied-orbital eigenvalues are approximations to *Ionization Potentials* (energy required to remove an electron)

Let $N^{(0)}$ be the GS for *N* particles : $(1\,,\,2\,,\,\ldots,i,\ldots,N)$

Let $(N-1,i)$ be the stationary state of *N-1* particles obtained removing electronic orbital *i* : $(1',2',\ldots,\cancel{i},\ldots,N')$

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Within HF we have $IP_i \approx E^{HF}(N-1,i) - E_0^{HF}(N)$

$$E_0^{HF}(N) = \sum_k h_k + \frac{1}{2}\sum_{jk} W_{jk}$$

$$\tilde{E}^{\,K}(N-1,i) = E_0^{HF}(N) - \varepsilon_i$$

Koopmans': neglect orbital relaxation

Koopmans' First Theorem

occupied-orbital eigenvalues are approximations to *Ionization Potentials* (energy required to remove an electron)

Let $N^{(0)}$ be the GS for *N* particles : $(1\,,\,2\,,\,\ldots,i,\ldots,N)$

Let $(N-1,i)$ be the stationary state of *N-1* particles obtained removing electronic orbital *i* : $(1',2',\ldots,\cancel{i},\ldots,N')$

The *Ionization Potential* is $IP_i = E(N-1,i) - E_0(N)$

Within HF we have $IP_i \approx E^{HF}(N-1,i) - E_0^{HF}(N)$

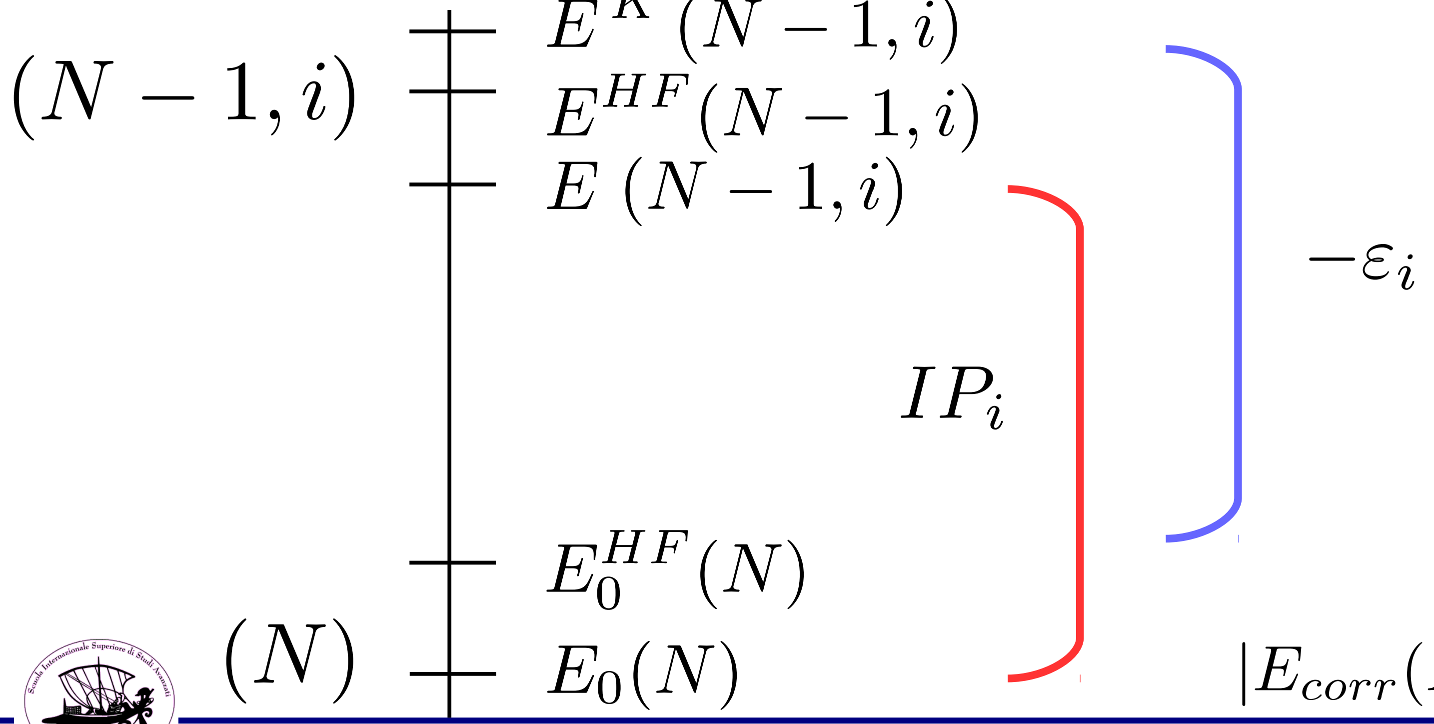
Koopmans' result $IP_i \approx -\varepsilon_i$

Koopmans' First Theorem

occupied-orbital eigenvalues are approximations to *Ionization Potentials* (energy required to remove an electron)

$$IP_i = E(N-1,i) - E_0(N) \approx E^{HF}(N-1,i) - E_0^{HF}(N)$$

$$\leq \tilde{E}^{K}(N-1,i) - E_0^{HF}(N) = -\varepsilon_i$$



$(N-1,i)$

$\tilde{E}^{K}(N-1,i)$

$E^{HF}(N-1,i)$

$E(N-1,i)$

$-\varepsilon_i$

IP_i

$E_0^{HF}(N)$

(N)

$E_0(N)$

$$IP_i \approx -\varepsilon_i$$

$$|E_{corr}(N-1)| \leq |E_{corr}(N)|$$

Koopmans' Second Theorem

unoccupied-orbital eigenvalues are approximations to *Electron Affinities* (energy gained by adding an electron)

Let $N^{(0)}$ be the GS for *N* particles : $(1\,,\,2\,,\,\ldots\,,N)$

Let $(N\!+\!1,\alpha)$ be the stationary state of *N+1* particles obtained adding electronic orbital α : $(1',2',\ldots,N',\alpha')$

The *Electron Affinity* is $EA_\alpha = E_0(N) - E(N+1,\alpha)$

Within HF we have $EA_\alpha \approx E_0^{HF}(N) - E^{HF}(N+1,\alpha)$

$$E_0^{HF}(N) = \sum_k h_k + \frac{1}{2}\sum_{jk} W_{jk}$$

Koopmans': neglect
orbital relaxation

$$E^{HF}(N+1,\alpha) = \sum_k h'_k + h'_\alpha + \frac{1}{2}\sum_{j,k} W'_{jk} + \sum_j W'_{j\alpha} \quad (\,W'_{\alpha\alpha} = 0\,)$$

Koopmans' Second Theorem

unoccupied-orbital eigenvalues are approximations to *Electron Affinities* (energy gained by adding an electron)

Let $N^{(0)}$ be the GS for *N* particles : $(1\,,\,2\,,\,\ldots\,,N)$

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The *Electron Affinity* is $EA_\alpha = E_0(N) - E(N+1,\alpha)$

Within HF we have $EA_\alpha \approx E_0^{HF}(N) - E^{HF}(N+1,\alpha)$

$$E_0^{HF}(N) = \sum_k h_k + \frac{1}{2}\sum_{jk} W_{jk}$$

Koopmans': neglect orbital relaxation

$$\tilde{E}^{\,K}(N+1,\alpha) = \sum_k h_k + h_\alpha + \frac{1}{2}\sum_{j,k} W_{jk} + \sum_j W_{j\alpha} \qquad (\,W_{\alpha\alpha} = 0\,)$$

Koopmans' Second Theorem

unoccupied-orbital eigenvalues are approximations to *Electron Affinities* (energy gained by adding an electron)

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$$E_0^{HF}(N) = \sum_k h_k + \frac{1}{2}\sum_{jk} W_{jk}$$

Koopmans': neglect orbital relaxation

$$\tilde{E}^{\,K}(N+1,\alpha) = E_0^{HF}(N) + h_\alpha + \sum_j W_{j\alpha}$$

Koopmans' Second Theorem

unoccupied-orbital eigenvalues are approximations to *Electron Affinities* (energy gained by adding an electron)

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Within HF we have $EA_\alpha \approx E_0^{HF}(N) - E^{HF}(N+1,\alpha)$

$$E_0^{HF}(N) = \sum_k h_k + \frac{1}{2}\sum_{jk} W_{jk}$$

Koopmans': neglect orbital relaxation

$$\tilde{E}^{\,K}(N+1,\alpha) = E_0^{HF}(N) + \varepsilon_\alpha$$

Koopmans' Second Theorem

unoccupied-orbital eigenvalues are approximations to *Electron Affinities* (energy gained by adding an electron)

Let $N^{(0)}$ be the GS for *N* particles : $(1\,,\,2\,,\,\ldots\,,N)$

Let $(N\!+\!1,\alpha)$ be the stationary state of *N+1* particles obtained adding electronic orbital α : $(1',2',\ldots,N',\alpha')$

The *Electron Affinity* is $EA_\alpha = E_0(N) - E(N+1,\alpha)$

Within HF we have $EA_\alpha \approx E_0^{HF}(N) - E^{HF}(N+1,\alpha)$

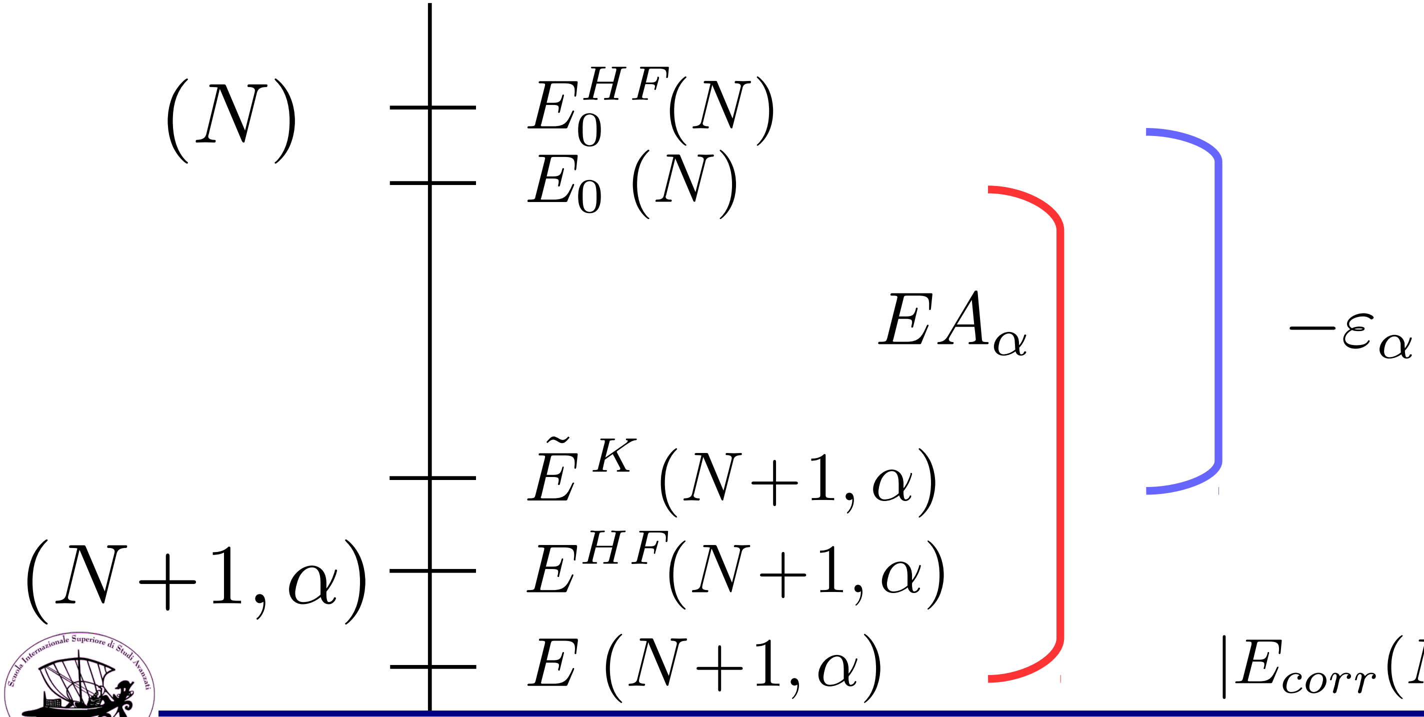
Koopmans' result $EA_\alpha \approx -\varepsilon_\alpha$

Koopmans' Second Theorem

unoccupied-orbital eigenvalues are approximations to *Electron Affinities* (energy gained by adding an electron)

$$EA_\alpha = E_0(N) - E(N+1,\alpha) \approx E_0^{HF}(N) - E^{HF}(N+1,\alpha)$$

$$\geq E_0^{HF}(N) - \tilde{E}^K(N+1,\alpha) = -\varepsilon_\alpha$$



(N)

$E_0^{HF}(N)$

$E_0\ (N)$

EA_α

$-\varepsilon_\alpha$

$\tilde{E}^K(N+1,\alpha)$

$(N+1,\alpha)$

$E^{HF}(N+1,\alpha)$

$E\ (N+1,\alpha)$

$$EA_\alpha > -\varepsilon_\alpha$$

$$|E_{corr}(N+1)| \geq |E_{corr}(N)|$$

Koopmans' Third Theorem

Eigenvalue differences are approximations to
(single particle) *Excitation Energies*

Let $N^{(0)}$ be the GS for N particles : $(1\,,\,2\,,\,\ldots,i,\ldots,N)$

Let $N^{*}_{(i\to\alpha)}$ be the stationary state of N particles where orbital i is promoted to orbital α : $(1',2',\ldots,\cancel{i},\ldots,N',\alpha')$

$$\Delta E^{i\to\alpha} = E(N^{*}_{(i\to\alpha)}) - E_0(N)$$

neglecting orbital relaxation

$$\Delta E^{i\to\alpha} \approx \sum_{k\neq i} h_k + h_\alpha + \frac{1}{2}\sum_{j,k\neq i} W_{j,k} + \sum_{j\neq i} W_{j\alpha} - \sum_{k} h_k - \frac{1}{2}\sum_{j,k} W_{j,k}$$

Koopmans' Third Theorem

Eigenvalue differences are approximations to
(single particle) *Excitation Energies*

Let $N^{(0)}$ be the GS for N particles : $(1\,,\,2\,,\,\ldots,i,\ldots,N)$

Let $N^{*}_{(i\to\alpha)}$ be the stationary state of N particles where orbital i is promoted to orbital α : $(1',2',\ldots,\cancel{i,}\ldots,N',\alpha')$

$$\Delta E^{i\to\alpha} = E(N^{*}_{(i\to\alpha)}) - E_0(N)$$

neglecting orbital relaxation

$$\Delta E^{i\to\alpha} \approx -h_i + h_\alpha + \frac{1}{2}\sum_{j,k\neq i} W_{j,k} + \sum_{j\neq i} W_{j\alpha} - \frac{1}{2}\sum_{j,k} W_{j,k}$$

Koopmans' Third Theorem

Eigenvalue differences are approximations to (single particle) *Excitation Energies*

Let $N^{(0)}$ be the GS for *N* particles : $(1\,,\,2\,,\,\ldots,i,\ldots,N)$

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$$\Delta E^{i\to\alpha} = E(N^{*}_{(i\to\alpha)}) - E_0(N)$$

neglecting orbital relaxation

$$\Delta E^{i\to\alpha} \approx \; -h_i \; +h_\alpha \; + \cancel{\frac{1}{2}\sum_{j,k\neq i} W_{j,k}} + \sum_{j\neq i} W_{j\alpha}$$

$$- \; \cancel{\frac{1}{2}\sum_{j,k\neq i} W_{j,k}} - \sum_{j} W_{j,i}$$

Koopmans' Third Theorem

Eigenvalue differences are approximations to
(single particle) *Excitation Energies*

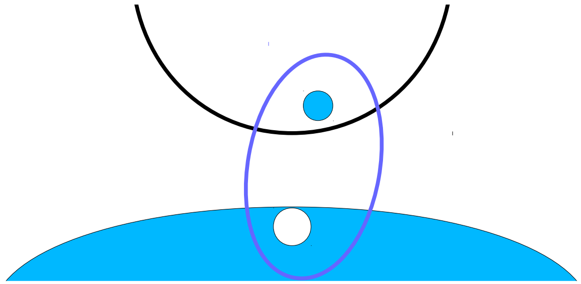
Let $N^{(0)}$ be the GS for *N* particles : $(1\,,\,2\,,\,\ldots,i,\ldots,N)$

Let $N^*_{(i\to\alpha)}$ be the stationary state of *N* particles where orbital i is promoted to orbital α : $(1',2',\ldots,\cancel{i},\ldots,N',\alpha')$

$$\Delta E^{i\to\alpha} = E(N^*_{(i\to\alpha)}) - E_0(N)$$

neglecting orbital relaxation

$$\Delta E^{i\to\alpha} \approx \varepsilon_\alpha - \varepsilon_i \boxed{- W_{i\alpha}}$$



e-h interaction
excitonic effects

neglecting it is *very bad* for localized excitations

atomic examples

The system has rotational symmetry and is spin independent
in Restricted HF the single particle wfcs are taken as

$$\phi_{nlm\sigma}(\mathbf{r}) = f_{nl}(r)\; Y_{lm}(\hat{r})\; \chi_\sigma$$

Hydrogen: $1s^1$ $E^{HF} = \varepsilon_{1s} = -1\ Ry$ ✓

Helium: $1s^2$ $E^{HF} = -5.723\ Ry,\quad E_0 = -5.807\ Ry,$

$$E_{corr} = -0.084\ Ry = -1.14\ eV$$

$I\ K:$ $\varepsilon_{1s} = -1.836\ Ry,\quad IP_1 = 1.807\ Ry$ ✓

$II\ K:$ no bound states above 1s => no negative ion ✓

$III\ K:$ no bound excitations ✗

atomic examples

Lithium: $1s^2 2s^1$

$$E^{HF} = -14.865\ Ry, \quad E_0 = IP_1 + IP_2 + IP_3 = -14.954\ Ry,$$

$$E_{corr} = -0.09\ Ry = -1.2\ eV$$

$I\ K:$ $\varepsilon_{2s} = -0.393\ Ry, \quad IP_1 = 0.396\ Ry$ ✓

Beryllium: $1s^2 2s^2$

$$E^{HF} = -29.146\ Ry, \quad E_0^{Th} = -29.335\ Ry, \ E_0^{Exp} = -29.339\ Ry,$$

$I\ K:$ $\varepsilon_{2s} = -0.618\ Ry, \quad IP_1 = 0.618\ Ry$ ✓ $E_{corr} = -2.6\ eV$

$\varepsilon_{1s} = -9.465\ Ry, \quad IP_{1s}^{Exp} = 8.9\ Ry$ ✓

$II\ K:$ no bound states above 2s => no negative ion ✓

atomic examples

… and so on filling the lowest eigenvalues according to the **Aufbau** principle $1s \to 2s \to 2p \to 3s \to 3p$

until *Potassium* (*K*, *Z*=19) is reached after *Argon* with electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6$

atomic examples

Potassium (*Z*=19)

	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^1$
$(1s)$	– 267.066	– 267.250
$(2s)$	– 28.980	– 29.161
$(2p)$	– 23.038	– 23.221
$(3s)$	– 3.498	– 3.671
$(3p)$	– 1.909	– 2.086
$(3d)$	*unbound*	– 0.116
$(4s)$	– 0.295	*unbound*
E_{tot}	– 599.165	– 599.076

atomic examples

... and so on filling the lowest eigenvalues according to the **Aufbau** principle $1s \to 2s \to 2p \to 3s \to 3p$

until *Potassium* (Z=19) is reached after *Argon* with electronic configuration $1s^2 2s^2 2p^6 3s^2 3p^6$

orbitals $4s$ and $3d$ have similar energy and HF correctly gives the $4s$ solution as more stable.

Thus *K:* $[Ar]4s^1$, then *Ca:* $[Ar]4s^2$, then *Sc:* $[Ar]4s^2 3d^1$

As it proceeds $3d$ becomes more localized than $4s$

atomic examples

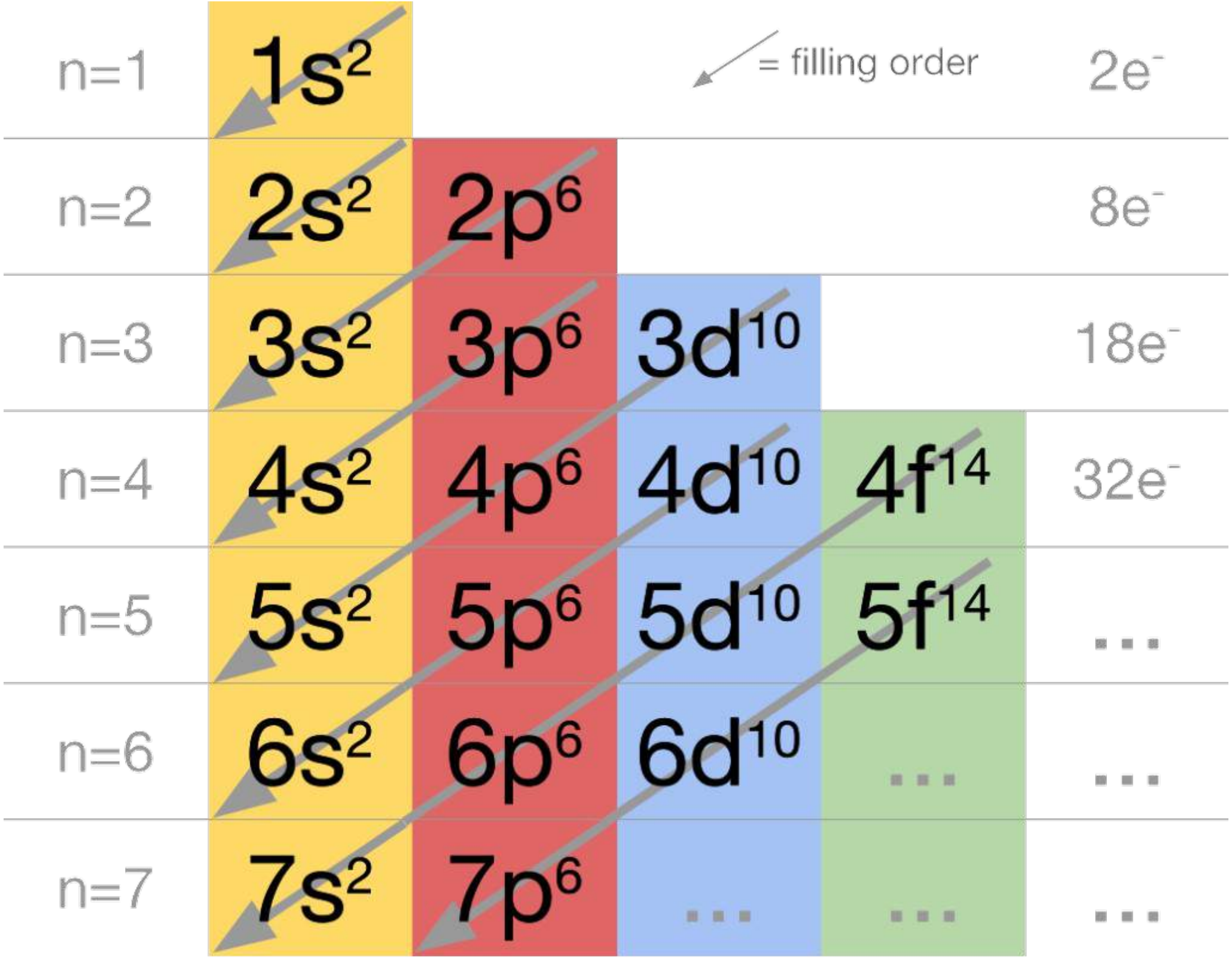
Titanium (Z=22) is a case of ***Anomalous Filling***

	$[Ar]4s^2 3d^2$	$[Ar]4s^1 3d^3$	$[Ar]3d^4$
$(3d)$	$-\ 0.812$	$-\ 0.483$	$-\ 0.289$
$(4s)$	$-\ 0.444$	$-\ 0.387$	*unbound*
E_{tot}	$-\ 1696.74$	$-\ 1696.62$	$-\ 1696.36$

It is an artifact of Restricted HF.
For completely **Unrestrited HF** *filling is always normal !*
V Bach, EH Lieb, M Loss, & JP Solovej, *PRL* **72**, 2981 (1994)

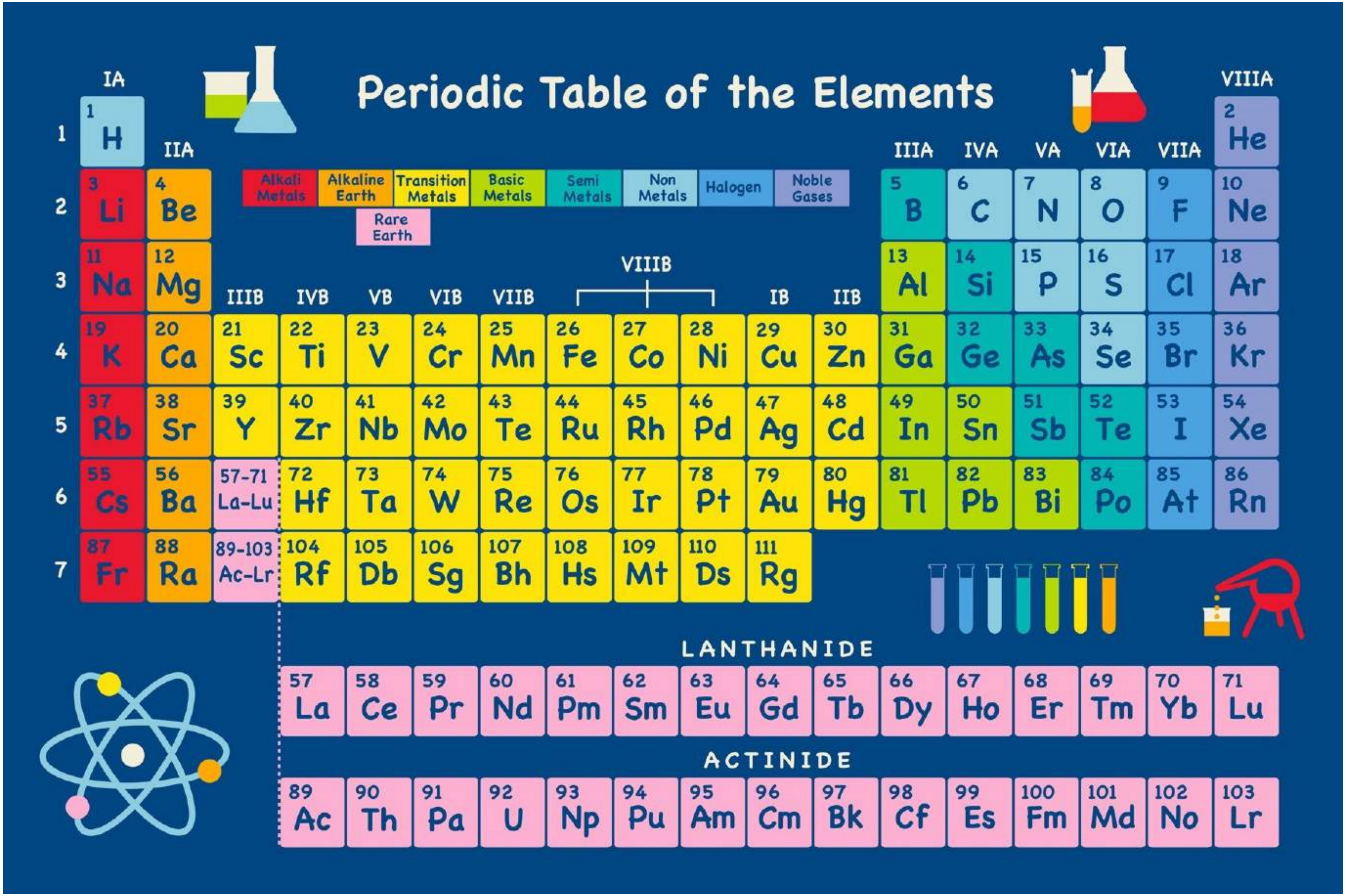
atomic examples

… and so on..



= filling order

n=1	$1s^2$				$2e^-$
n=2	$2s^2$	$2p^6$			$8e^-$
n=3	$3s^2$	$3p^6$	$3d^{10}$		$18e^-$
n=4	$4s^2$	$4p^6$	$4d^{10}$	$4f^{14}$	$32e^-$
n=5	$5s^2$	$5p^6$	$5d^{10}$	$5f^{14}$	...
n=6	$6s^2$	$6p^6$	$6d^{10}$	...	...
n=7	$7s^2$	$7p^6$	...	...	...



Periodic Table of the Elements

Alkali Metals · Alkaline Earth · Transition Metals · Basic Metals · Semi Metals · Non Metals · Halogen · Noble Gases · Rare Earth

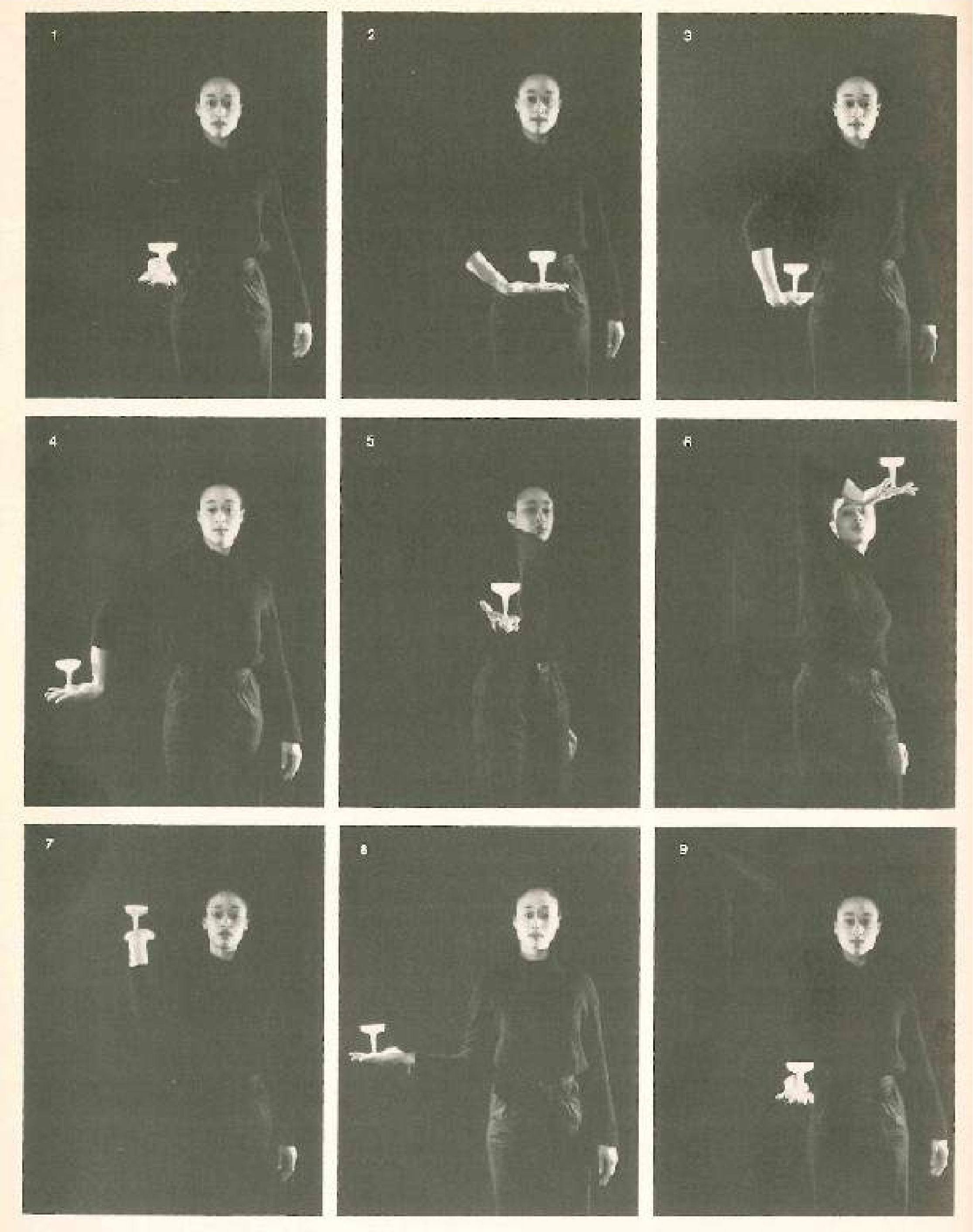
	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB	VIIIB	VIIIB	IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Te	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57-71 La-Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89-103 Ac-Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg							

LANTHANIDE

57	58	59	60	61	62	63	64	65	66	67	68	69	70	71
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu

ACTINIDE

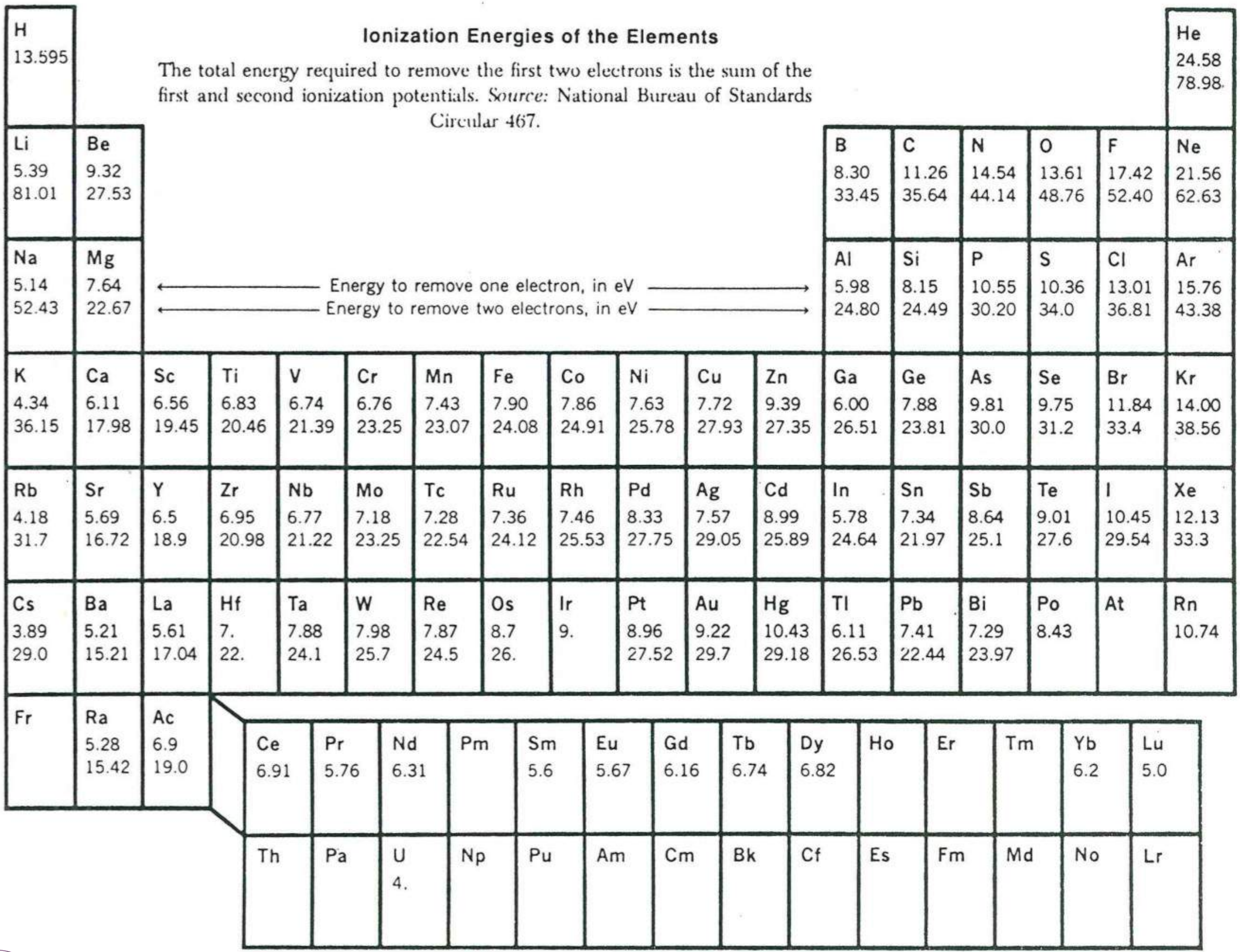
89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr



binasuan -
wineglass
philippino dance

Energy Conversion Factors

$1 \downarrow is \rightarrow$	$kcal/mole$	$kJ/mole$	$mRy/unit$	$meV/unit$
$kcal/mole$	1	4.184	3.187	43.364
$kJ/mole$	0.239	1	0.762	10.364
$mRy/unit$	0.3138	1.313	1	13.6058
$meV/unit$	0.02306	0.09649	0.073498	1



Ionization Energies of the Elements

The total energy required to remove the first two electrons is the sum of the first and second ionization potentials. *Source:* National Bureau of Standards Circular 467.

← Energy to remove one electron, in eV →
← Energy to remove two electrons, in eV →

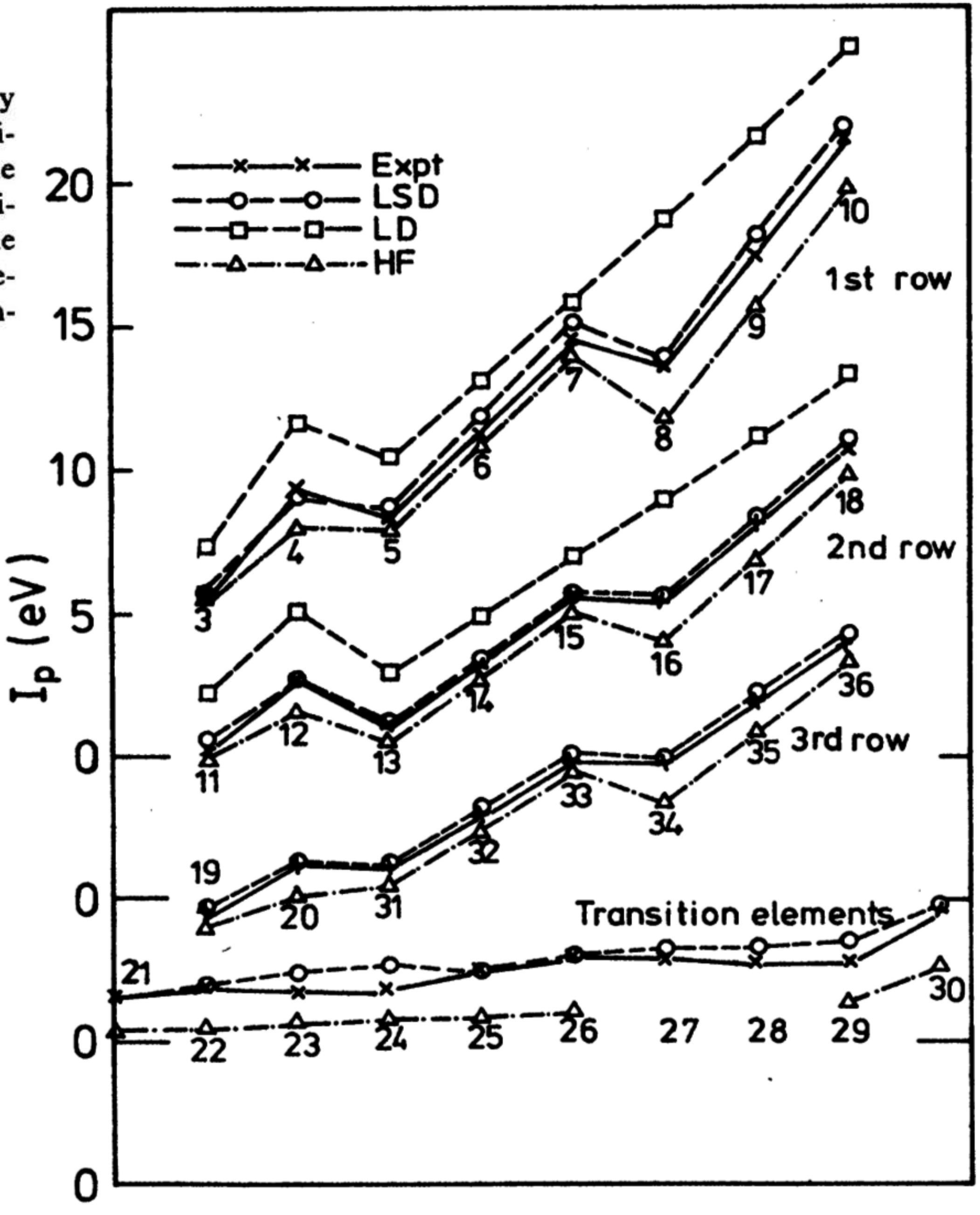
H 13.595																	He 24.58 78.98
Li 5.39 81.01	Be 9.32 27.53											B 8.30 33.45	C 11.26 35.64	N 14.54 44.14	O 13.61 48.76	F 17.42 52.40	Ne 21.56 62.63
Na 5.14 52.43	Mg 7.64 22.67											Al 5.98 24.80	Si 8.15 24.49	P 10.55 30.20	S 10.36 34.0	Cl 13.01 36.81	Ar 15.76 43.38
K 4.34 36.15	Ca 6.11 17.98	Sc 6.56 19.45	Ti 6.83 20.46	V 6.74 21.39	Cr 6.76 23.25	Mn 7.43 23.07	Fe 7.90 24.08	Co 7.86 24.91	Ni 7.63 25.78	Cu 7.72 27.93	Zn 9.39 27.35	Ga 6.00 26.51	Ge 7.88 23.81	As 9.81 30.0	Se 9.75 31.2	Br 11.84 33.4	Kr 14.00 38.56
Rb 4.18 31.7	Sr 5.69 16.72	Y 6.5 18.9	Zr 6.95 20.98	Nb 6.77 21.22	Mo 7.18 23.25	Tc 7.28 22.54	Ru 7.36 24.12	Rh 7.46 25.53	Pd 8.33 27.75	Ag 7.57 29.05	Cd 8.99 25.89	In 5.78 24.64	Sn 7.34 21.97	Sb 8.64 25.1	Te 9.01 27.6	I 10.45 29.54	Xe 12.13 33.3
Cs 3.89 29.0	Ba 5.21 15.21	La 5.61 17.04	Hf 7. 22.	Ta 7.88 24.1	W 7.98 25.7	Re 7.87 24.5	Os 8.7 26.	Ir 9.	Pt 8.96 27.52	Au 9.22 29.7	Hg 10.43 29.18	Tl 6.11 26.53	Pb 7.41 22.44	Bi 7.29 23.97	Po 8.43	At	Rn 10.74
Fr	Ra 5.28 15.42	Ac 6.9 19.0															
			Ce 6.91	Pr 5.76	Nd 6.31	Pm	Sm 5.6	Eu 5.67	Gd 6.16	Tb 6.74	Dy 6.82	Ho	Er	Tm	Yb 6.2	Lu 5.0	
			Th	Pa	U 4.	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

First Ionization Energies

FIG. 8. First ionization energy of atoms in the local-density (LD), local spin-density (LSD), and Hartree-Fock (HF) approximations compared with experiment. The numbers show the atomic numbers of the atoms considered. For reasons of clarity, the zero of energy is shifted by 5, 10, and 15 eV for the second row, the third row, and the transition-element row, respectively. The LD results for the first and second rows are increased by an additional 2 eV.

Rev. Mod. Phys., Vol. 61, No. 3, July 1989

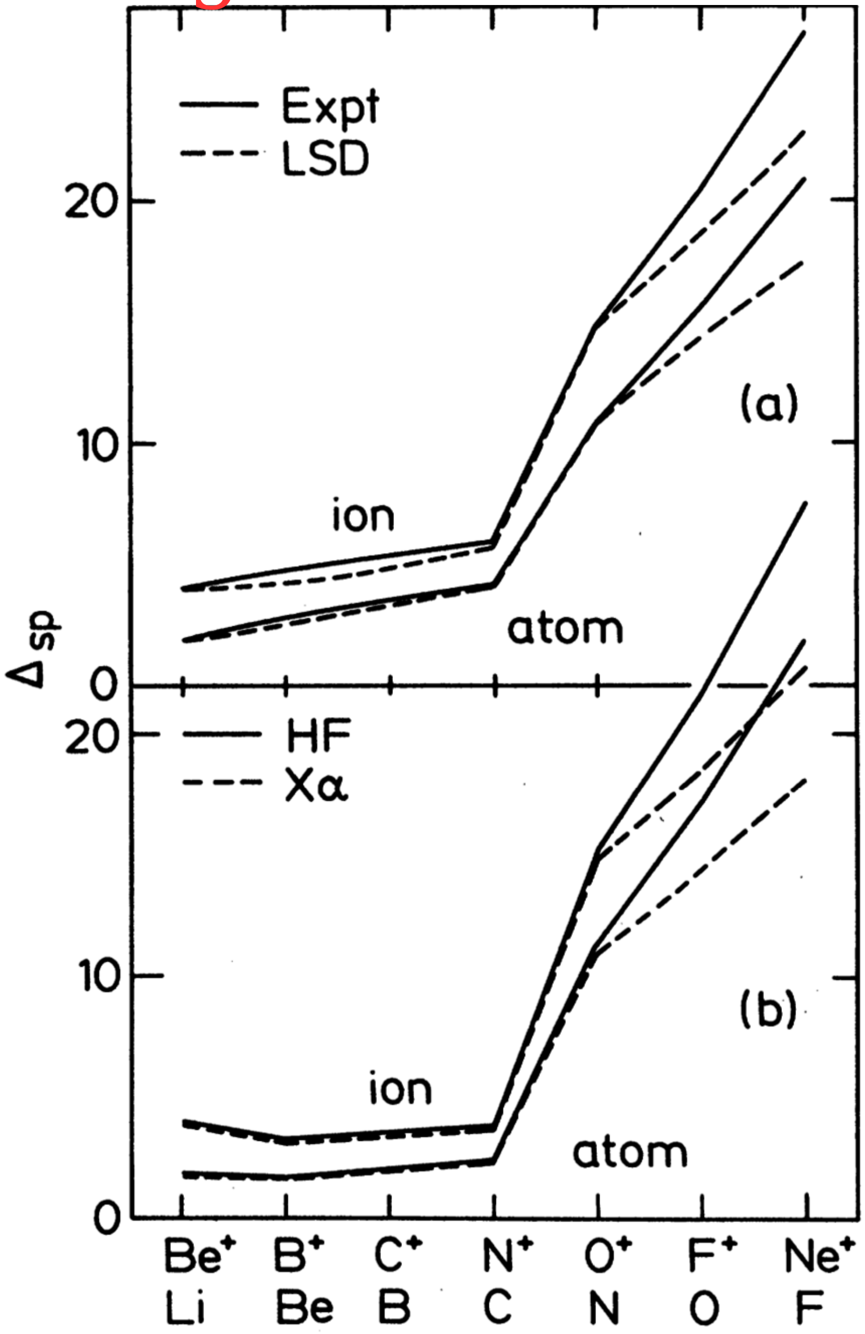
Jones & Gunnarsson



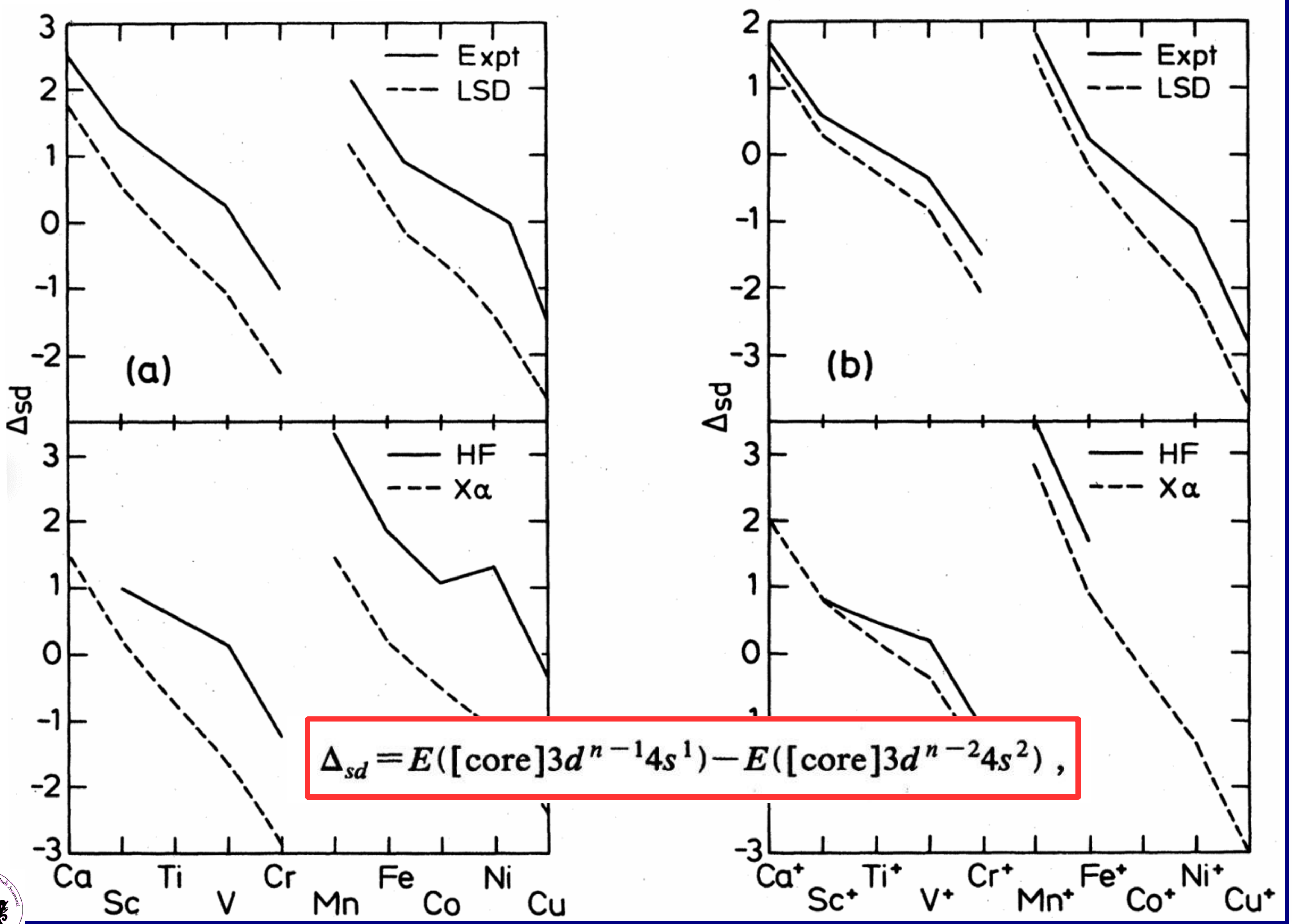
s-p Transfer Energies

FIG. 9. The *sp* transfer energies Δ_{sp} for the first-row atom ions: (a) experimental and local spin-density (LSD) result Hartree-Fock (HF) and $X\alpha$ results. The energies are in eV.

$$\Delta_{sp} = E(1s^2 2s 2p^{n-1}) - E(1s^2 2s^2 2p^{n-2}) \; ,$$

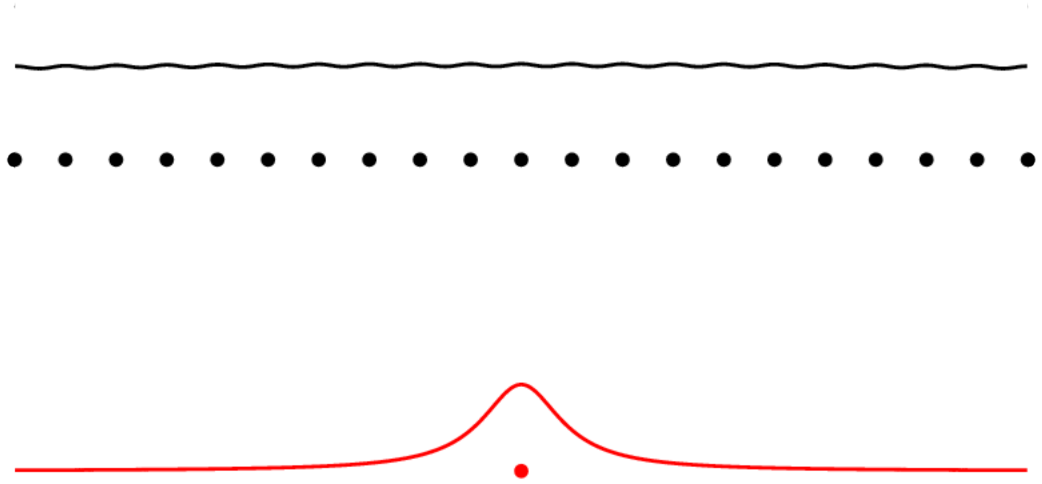


s-d Transfer Energies



$$\Delta_{sd} = E([\text{core}]3d^{n-1}4s^{1}) - E([\text{core}]3d^{n-2}4s^{2}) \ ,$$

Homogeneous Electron Gas



Consider a periodic system of electrons and ions (neutral)

and let's smear the ionic charge distribution

the external potential tends to a constant (-infinity)

Hartree-Fock in the HEG

$$\mathcal{H}_{el}(\mathbf{R}) = \sum_{i=1}^{N} \frac{p_i^2}{2m_e} + \frac{1}{2} \sum_{\substack{i,j \\ i \neq j}}^{N} \frac{e^2}{|r_i - r_j|} - \sum_{i}^{N} \int \rho_{ion}(r') \frac{e^2}{|r' - r_i|}\, dr'$$

$$+ \frac{1}{2} \int \rho_{ion}(r) \frac{e^2}{|r - r'|} \rho_{ion}(r')\, dr dr'$$

In the Jellium model (homogeneous electron gas) the ionic density is *uniform* and the system is *neutral*

$$\rho_{ion}(r) = n = \frac{N}{V}$$

The system is translational invariant w/o ext magnetic field
It is *postulated* that so is the HF scf hamiltonian (to be verif).
HF wfcs are therefore just plane waves.

$$\psi_{k,\sigma}(r) = \frac{1}{\sqrt{V}} e^{+ikr} |\sigma\rangle$$

Hartree-Fock in the HEG

The system is translational invariant w/o ext magnetic field
It is *postulated* that so is the HF scf hamiltonian (to be verif).
HF wfcs are therefore just plane waves.

$$\psi_{k,\sigma}(r) = \frac{1}{\sqrt{V}} e^{+ikr} |\sigma\rangle$$

The density is uniform

$$\rho_{el}(r) = \sum_{\sigma} \sum_{|k|<k_F} |\psi_{k,\sigma}(r)|^2 = \frac{2}{V} \sum_{|k|<k_F} 1 \qquad \sum_{k} \to \frac{V}{(2\pi)^3} \int d^3k$$

$$= \frac{V}{(2\pi)^3} \frac{2}{V} \int_{|k|<k_F} d^3k = \frac{2}{(2\pi)^3} 4\pi \int_0^{k_F} k^2 dk = \frac{k_F^3}{3\pi^2} \overset{\uparrow}{=} n$$

neutrality

$$\rho_{\uparrow}(r) = \rho_{\downarrow}(r) = \frac{n}{2} \longleftarrow \text{non magnetic sol.}$$

Hartree-Fock in the HEG

$$\rho_{el}(r) = \rho_{ion}(r) = n$$

The total electrostatic energy of jellium is zero

$$E_{tot.e.s.} = E_H + E_{el-ion} + E_{ion-ion}$$

$$E_{tot.e.s.} =$$

$$\frac{e^2}{2}\int \frac{\rho_{el}(r)\rho_{el}(r')}{|r-r'|}drdr' - e^2\int \frac{\rho_{el}(r)\rho_{ion}(r')}{|r-r'|}drdr' + \frac{e^2}{2}\int \frac{\rho_{ion}(r)\rho_{ion}(r')}{|r-r'|}drdr'$$

$$= \frac{e^2}{2}\int \frac{\rho_{tot}(r)\rho_{tot}(r')}{|r-r'|}drdr' = 0$$

Hartree-Fock in the HEG

In general ...

$$E_{tot.e.s.} = \frac{e^2}{2}\int \frac{\rho_{tot}(r)\rho_{tot}(r')}{|r-r'|} dr dr'$$

$$\nabla \cdot \mathbf{E}(r) = e\,\rho_{tot}(r), \qquad \nabla^2 \frac{1}{|r-r'|} = -4\pi\,\delta(r-r')$$

$$E_{tot.e.s.} = \frac{1}{8\pi}\int |\mathbf{E}(r)|^2 dr$$

$$\rho_{tot}(r) = 0 \quad \Longrightarrow \quad \nabla \cdot \mathbf{E}(r) = 0 \quad \Longrightarrow \quad \mathbf{E}(r) = const$$

in metals the field is completely screaned

no macroscopic electric field in insulating samples

Hartree-Fock in the HEG

$$E_{tot.e.s.} = E_H + E_{el-ion} + E_{ion-ion} = 0$$

For the same reason

$$V_{tot.e.s.}(r) = V_{ion}(r) + V_H(r)$$

$$= -e^2 \int \frac{\rho_{ion}(r')}{|r-r'|} dr' + e^2 \int \frac{\rho_{el}(r')}{|r-r'|} dr' = e^2 \int \frac{\rho_{tot}(r')}{|r-r'|} dr' = 0$$

The average value of the electrostatic potential is actually <u>*arbitrary*</u> and is *conventionally* set to zero.

There is no simple way to compare the eigenvalues of two different periodic calculations.

Hartree-Fock in the HEG

Exchange potential:

$$V_x\psi_{k\sigma}(r) = -\sum_{\sigma'}\sum_{k'}\psi_{k'\sigma'}(r)\int \underbrace{\psi^*_{k'\sigma'}(r')\frac{e^2}{|r-r'|}\psi_{k\sigma}(r)}_{\delta_{\sigma\sigma'}}d^3r'$$

$$= -\sum_{|k'|<k_F}\frac{1}{V^{\frac{3}{2}}}e^{+ik'r}\int e^{-i(k'-k)r'}\frac{e^2}{|r-r'|}d^3r'\ |\sigma\rangle$$

$$= \left[-\sum_{|k'|<k_F}\frac{1}{V}\int e^{-i(k'-k)(r'-r)}\frac{e^2}{|r-r'|}d^3r'\right]\frac{e^{+ikr}}{\sqrt{V}}|\sigma\rangle$$

Hartree-Fock in the HEG

Exchange potential:

$$V_x \psi_{k\sigma}(r) = \left[- \sum_{|k'|<k_F} \frac{1}{V} \int e^{-i(k'-k)(r'-r)} \frac{e^2}{|r-r'|} d^3r' \right] \psi_{k\sigma}(r)$$

$$= \underbrace{\left[- \sum_{|k'|<k_F} V(k-k') \right]}_{\text{a k-dependent constant}} \psi_{k\sigma}(r)$$

where $V(q) = \frac{1}{V} \int \frac{e^2}{|r|} e^{-iqr} d^3r = \frac{1}{V} \frac{4\pi e^2}{q^2}$

Hartree-Fock in the HEG

Exchange potential:

$$V_x \psi_{k\sigma}(r) = \left[- \sum_{|k'|<k_F} V(k-k') \right] \psi_{k\sigma}(r)$$

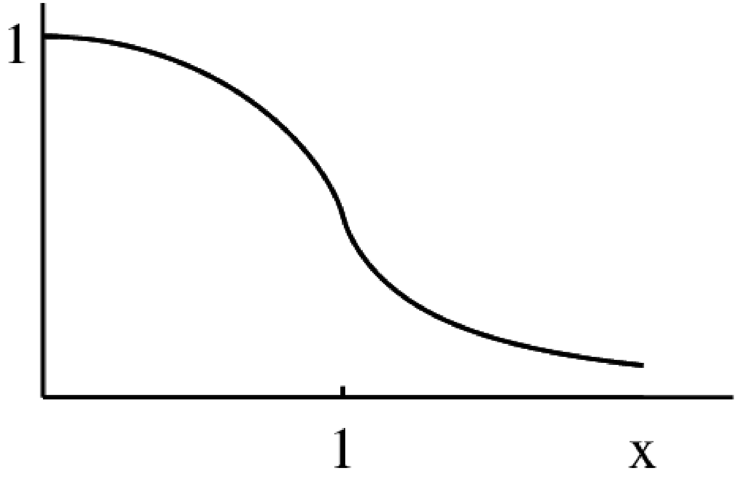
This integral is done, for instance, in Kittel "QTofS"

$$\frac{1}{V} \sum_{|k'|<k_F} \frac{4\pi e^2}{|k-k'|^2} = \frac{1}{(2\pi)^3} \int_{|k'|<k_F} d^3k' \frac{4\pi e^2}{|k-k'|^2} = \frac{2e^2}{\pi} k_F F(k/k_F)$$

Where F is the Lindhard function

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

$$F(0) = 1, \quad F(1) = 1/2,$$
$$F'(1) = -\infty$$

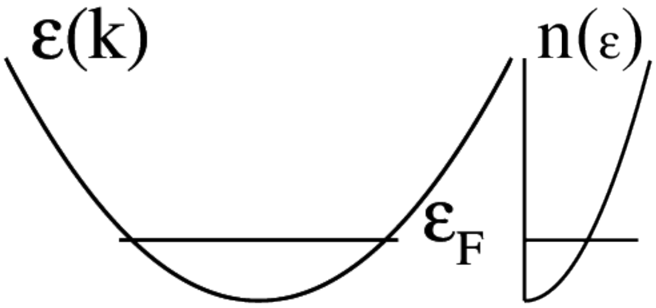


Hartree-Fock in the HEG

$$\left[-\frac{\hbar^2}{2m}\nabla^2-\frac{2e^2}{\pi}k_F F(k/k_F)\right]\psi_{k\sigma}(r)=\varepsilon_{k\sigma}\psi_{k\sigma}(r)$$

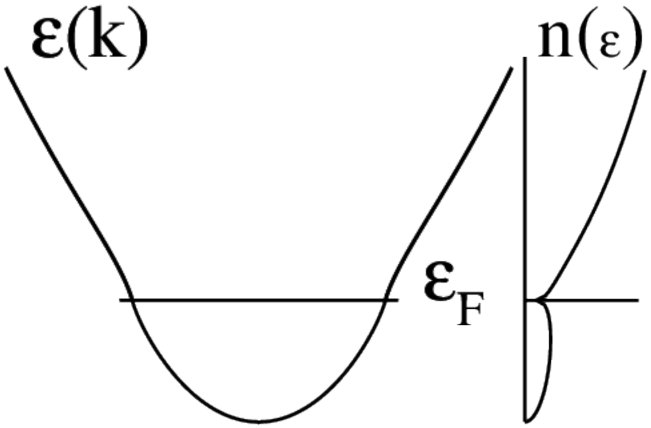
$$\varepsilon_{k\sigma}=\frac{\hbar^2k^2}{2m}-\frac{2e^2}{\pi}k_F F(k/k_F)$$

$$k_F=\left(3\pi^2 n\right)^{1/3}$$



for $n \longrightarrow \infty$

kinetic energy dominates



at any finite density *n*

$n(\varepsilon_F)=0$

Slater approximation for Vx

In the HEG the exch. potential is a simple function of *n* (and *k*)

$$V_x(k,\sigma) = -\frac{2e^2}{\pi} k_F F(k/k_F) = -4e^2 \left(\frac{3\,n_\sigma}{4\pi}\right)^{1/3} F(k/k_F)$$

Slater approx is to apply it locally with some effective *F*

$$V_x(r,\sigma) = -4e^2 \left(\frac{3\,n_\sigma(r)}{4\pi}\right)^{1/3} \tilde{F}$$

1) average over the occupied states

$$\tilde{F} = \langle F \rangle = \frac{3}{4\pi}\int_{|x|<1} F(x) d^3x \;=\; 3\int_0^1 x^2 F(x) dx = 3/4$$

$$V_x(r,\sigma) = -3e^2 \left(\frac{3\,n_\sigma(r)}{4\pi}\right)^{1/3}$$

2) value good for the Fermi energy

$$\tilde{F} = F(k_F/k_F) = 1/2$$

$$V_x(r,\sigma) = -2e^2 \left(\frac{3\,n_\sigma(r)}{4\pi}\right)^{1/3}$$

Slater approximation for Vx

In the HEG the exch. potential is a simple function of *n* (and *k*)

$$V_x(k,\sigma) = -\frac{2e^2}{\pi} k_F F(k/k_F) = -4e^2 \left(\frac{3\, n_\sigma}{4\pi}\right)^{1/3} F(k/k_F)$$

Slater approx is to apply it locally with some effective *F*

$$V_x(r,\sigma) = -4e^2 \left(\frac{3\, n_\sigma(r)}{4\pi}\right)^{1/3} \tilde{F} \qquad \text{with} \qquad \frac{1}{2} < \tilde{F} < \frac{3}{4}$$

or $$V_x(r,\sigma) = -3e^2\, \alpha \left(\frac{3\, n_\sigma(r)}{4\pi}\right)^{1/3} \qquad \text{with} \qquad \frac{2}{3} < \alpha < 1$$

In the X_α method α is used as a parameter to generate orbitals to be used in the HF energy evaluation

Hartree-Fock in the HEG

$$\left[-\frac{\hbar^2}{2m}\nabla^2 - \frac{2e^2}{\pi}k_F F(k/k_F)\right]\psi_{k\sigma}(r) = \varepsilon_{k\sigma}\psi_{k\sigma}(r)$$

$$\varepsilon_{k\sigma} = \frac{\hbar^2 k^2}{2m} - \frac{2e^2}{\pi}k_F F(k/k_F)$$

Total energy is

$$\begin{aligned}
\frac{E_{tot}}{N} &= \frac{1}{N}\left[\sum_{\sigma}\sum_{|k|<k_F}\langle\psi_{k\sigma}| -\frac{\hbar^2}{2m}\nabla^2|\psi_{k\sigma}\rangle - \frac{1}{2}\sum_{\sigma}\sum_{|k|<k_F}\langle\psi_{k\sigma}|V_x|\psi_{k\sigma}\rangle\right] \\
&= \frac{1}{N}\left[2\sum_{|k|<k_F}\frac{\hbar^2k^2}{2m} - \frac{1}{2}2\sum_{|k|<k_F}\frac{2e^2}{\pi}k_F F(k/k_F)\right] \\
&= \frac{V}{N}\frac{1}{(2\pi)^3}\left[2\frac{\hbar^2}{2m}\int_{|k|<k_F}k^2\, d^3k - \frac{2e^2}{\pi}k_F^4\int_{|k|<k_F}d^3k\,\frac{1}{k_F^3}F(k/k_F)\right]
\end{aligned}$$

Hartree-Fock in the HEG

Total energy is

$$\frac{E_{tot}}{N} = \frac{V}{N}\frac{1}{(2\pi)^3}\left[2\frac{\hbar^2}{2m}\int_{|k|<k_F} k^2\, d^3k - \frac{2e^2}{\pi}k_F^4\int_{|k|<k_F} d^3k\,\frac{1}{k_F^3}F(k/k_F)\right]$$

$$= \frac{1}{n}\left[\frac{4\pi}{(2\pi)^3}\frac{\hbar^2}{m}\frac{k_F^5}{5} - \frac{8e^2}{(2\pi)^3}k_F^4\underbrace{\int_0^1 x^2F(x)dx}_{1/4}\right]$$

$$\frac{E_{tot}}{N} = \frac{3}{5}\frac{\hbar^2}{2m}k_F^2 - \frac{3e^2}{4\pi}k_F = \left(\frac{2.21}{r_s^2} - \frac{0.916}{r_s}\right) Ry$$

where $k_F = (3\pi^2 n)^{1/3}$

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

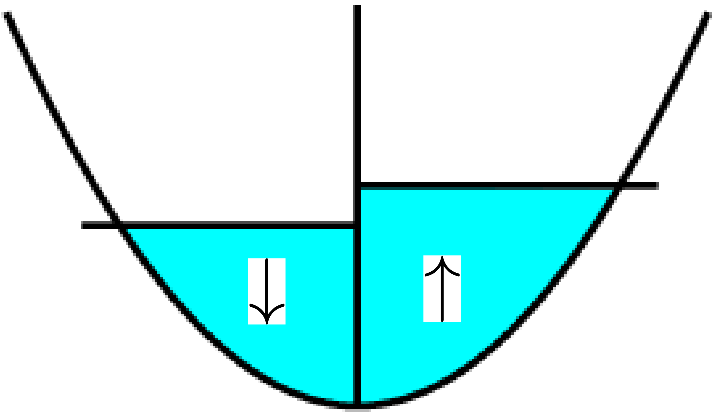
Hartree-Fock in the HEG

The *homogenous spin compensated* solution is self-consistent but is not the only possible solution

There can be *homogeneous paramagnetic* solutions

$$n = n_\uparrow + n_\downarrow, \quad \zeta = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}, \qquad n_\uparrow = \frac{1+\zeta}{2} n, \;\; n_\downarrow = \frac{1-\zeta}{2} n$$

$$k_{F\uparrow} = (6\pi^2 n_\uparrow)^{1/3}, \quad k_{F\downarrow} = (6\pi^2 n_\downarrow)^{1/3}$$



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$$n = n_\uparrow + n_\downarrow, \quad \zeta = \frac{n_\uparrow - n_\downarrow}{n_\uparrow + n_\downarrow}, \qquad n_\uparrow = \frac{1+\zeta}{2} n, \;\; n_\downarrow = \frac{1-\zeta}{2} n$$

$$k_{F\uparrow} = (6\pi^2 n_\uparrow)^{1/3}, \quad k_{F\downarrow} = (6\pi^2 n_\downarrow)^{1/3}$$

$$\frac{E_{kin}}{N}(n,\zeta) = \frac{3}{5}\frac{\hbar^2}{2m}(3\pi^2 n)^{2/3}\left[\frac{(1+\zeta)^{5/3} + (1-\zeta)^{5/3}}{2}\right]$$

$$\frac{E_x}{N}(n,\zeta) = -\frac{2e^2}{\pi}(3\pi^2 n)^{1/3}\left[\frac{(1+\zeta)^{4/3} + (1-\zeta)^{4/3}}{2}\right]$$

Hartree-Fock in the HEG

Non Magn
solution

$$\frac{E_{tot}}{N}(n,\zeta=0) \;=\; \left(\frac{2.21}{r_s^2}-\frac{0.916}{r_s}\right)\;Ry$$

Magnetic
solution

$$\frac{E_{tot}}{N}(n,\zeta=1) \;=\; \left(\frac{2.21}{r_s^2}2^{2/3}-\frac{0.916}{r_s}2^{1/3}\right)\;Ry$$

$$r_s > 5.45\;a_0$$

$$E_{tot}(\zeta=1)\;<\;E_{tot}(\zeta=0)$$

if correlation is included one needs $r_s\;>\;26\;\div\;75\;\;a_0$

in typical alkali metals $r_s\;\approx 3.2 \div 5.6\;\;a_0$ $\qquad 1.9 \div 3.7\;\;a_0$

Li *Cs* *Be* *Ba*

simple metals are not magnetic

Stoner Criterium for Ferromagnetism

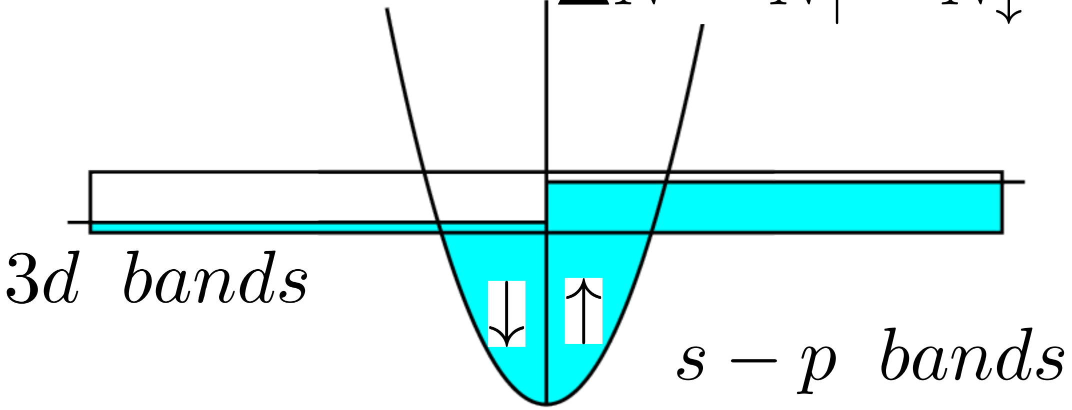
However ...

$$\textit{Fe}: \qquad r_s = 2.12 \ a_0$$

Still *Fe* is magnetic and so are *Cr, Ni, Co*

How is it so ?

$$\Delta N = N_\uparrow - N_\downarrow$$



$$\Delta E_{kin} \approx \frac{\Delta\varepsilon \Delta N}{2} \approx \frac{\Delta N^2}{2n(\varepsilon_F)}$$

$$\Delta E_x \approx -I_x \frac{\Delta N^2}{2}$$

$$\Delta E_{kin} + \Delta E_x < 0$$

$$n(\varepsilon_F) I_x > 1$$

Broken Symmetry solutions in the HEG

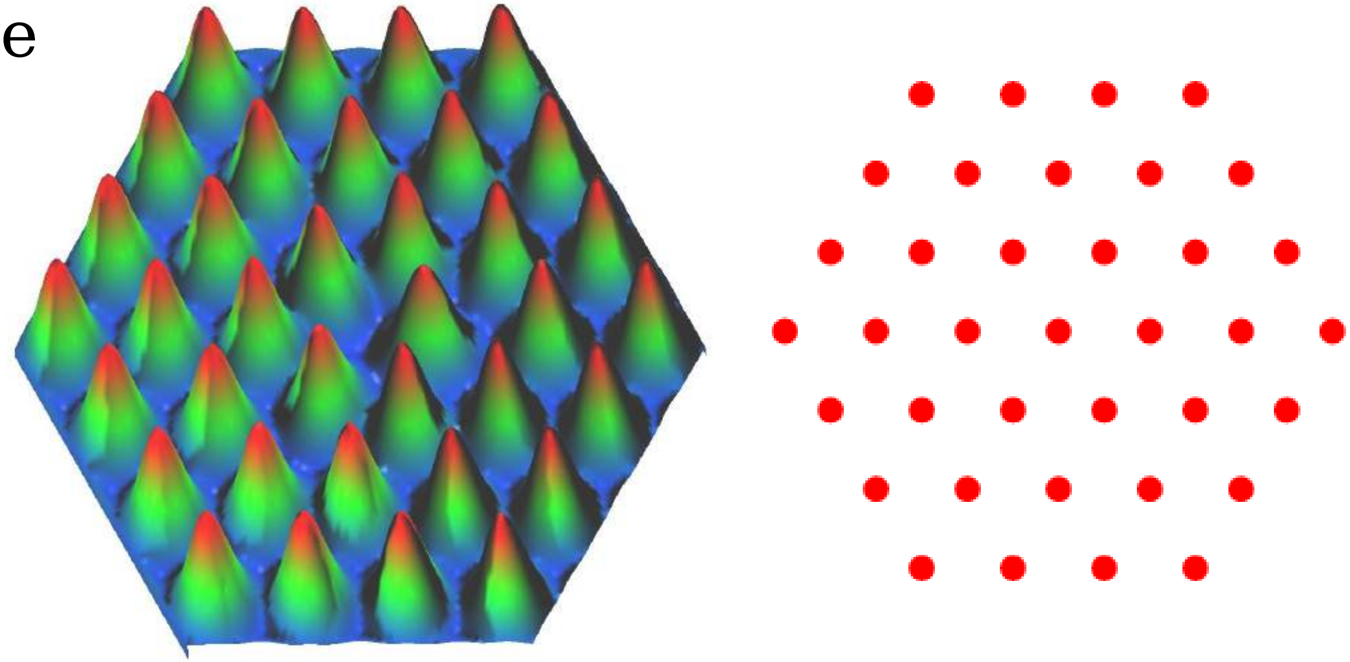
The *homogenous spin compensated* solution is self-consistent but is not the only possible solution

There can be *homogeneous paramagnetic* solutions

At even lower density (larger r_s), where kinetic energy is not relevant anymore, there are *non homogeneous* solutions that become competitive

$$r_s > 106\ a_0$$

Wigner crystal:



Broken Symmetry solutions in the HEG

Wigner crystal wfc:

$$\Phi^{wc}(r_1, ..., r_N) \approx \mathcal{A}[\phi(r_1 - R_1)\cdots\phi(r_N - R_N)]$$

where $$\phi(r) = (\frac{\alpha}{\pi})^{3/4}\exp(-\frac{\alpha r^2}{2})$$

and $\{R_I\}$ are the lattice sites of the electronic crystal

Ewald Sums

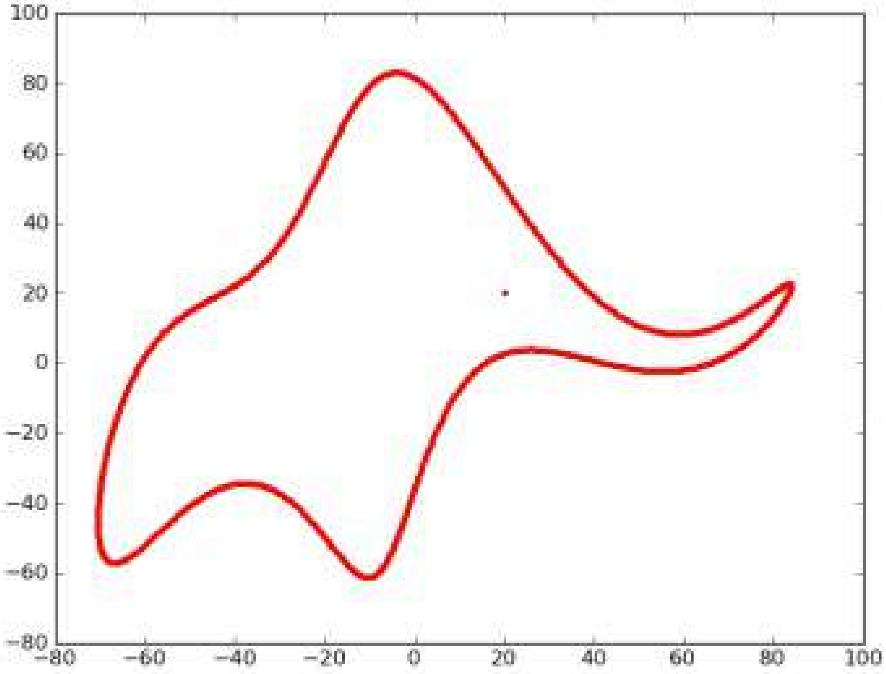
Electrostatic energy of a lattice of point charges in a neutralizing uniform background.

$$\sum_{R\neq 0}\frac{e^2}{|R|}-\int\frac{ne^2}{|r|}dr \quad\leftrightarrow\quad \frac{1}{\Omega}\sum_{G\neq 0}\frac{4\pi e^2}{G^2}$$

$$\frac{1}{|R|}=\frac{\mathtt{erf}(\sqrt{\alpha}|R|)}{|R|}+\boxed{\frac{\mathtt{erfc}(\sqrt{\alpha}|R|)}{|R|}}$$

$$\frac{1}{G^2}=\boxed{\frac{\mathtt{exp}(-G^2/4\alpha)}{G^2}}+\frac{1-\mathtt{exp}(-G^2/4\alpha)}{G^2}$$

MP Tosi in *Solid State Physics* ***16***, *p.1*



A turning point in Freeman Dyson's life occurred during a meeting in the Spring of 1953 when Enrico Fermi criticized the complexity of Dyson's model by quoting Jhonny von Neumann:" With four parameters I can fit an elephant, ..."

J Mayer, K Khairy, & J Howard, *Am J Phys* **78**, 648 (2010)

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THE END