Chapter 7: Mean-field approximation: static Hartree-Fock theory and density functional theory

Mean-field approximation is most important in

- atomic physics
- nuclear physics
- condensed matter / quantum chemistry

Basic idea:

given 2-body interactions

$$V^{(2)} = \frac{1}{2} \sum_{\substack{i,j=1 \\ (i \neq j)}}^{N} v^{(2)}(x_i, x_j)$$

↓ simplifying assumption: $|\Phi_0\rangle$ = single Slater determinant

derive 1-body "mean field" potential

$$V^{(1)}_{\text{m.f.}} = \sum_{i=1}^{N} v^{(1)}(x_i)$$

which describes the given 2-body interactions "on average". Mathematically much easier to handle! Mean-field approximations turn out to be surprisingly good!

ch. 7.1 **General N-body problem: time-dep. Schrödinger eq. in coord. space and in occupation # space**

Ref: Fetter & Walecka, ch. 1.1

a) in coord. space

$$H(x_1,\dots,x_N) = T^{(1)} + V^{(1)} + V^{(2)} + V^{(3)} + \dots \quad \text{Hamiltonian}$$

$T^{(1)}$ = kin. energy $= \sum_{i=1}^{N} -\frac{\hbar^2}{2m}\nabla_i^2$ = one-body op.

$V^{(1)}$ = external one-body potential $= \sum_{i=1}^{N} V^{(1)}(x_i)$

$V^{(2)}$ = two-body interaction $= \frac{1}{2}\sum_{\substack{i,j=1 \\ (i\neq j)}}^{N} V^{(2)}(x_i,x_j)$

⋮ etc.

time-dep. Schrödinger eq.

In the most general case, the potentials may be time-dep., in particular $V^{(1)}(t)$, e.g. external time-dep. field.

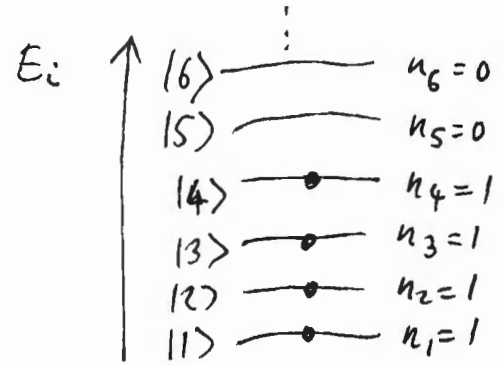
$$\left[H(x_1,\dots,x_N) - i\hbar\frac{\partial}{\partial t}\right]\psi(x_1,\dots,x_N;t) = 0$$

For fermions, the set of all possible Slater determinants with N occupied s.p. levels form a complete set, so we can expand ψ as follows

$$\psi(x_1,\dots,x_N;t) = \sum_{n_1,n_2,\dots,n_\infty=0}^{(1)} f(n_1,n_2,\dots,n_\infty;t)\,\phi_{n_1,n_2,\dots n_\infty}(x_1,\dots,x_N)$$

ψ: exact many-body WF; f: configuration amplitude; ϕ: Slater det.

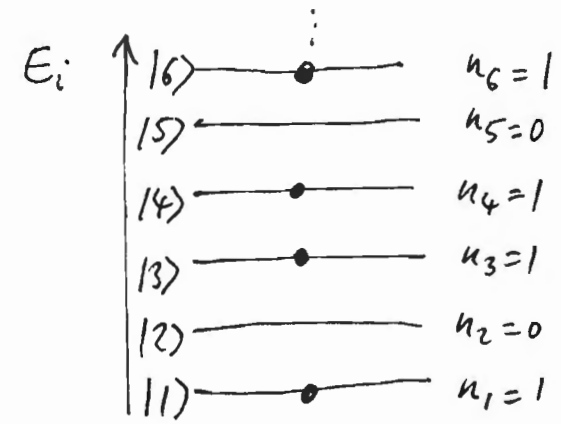
We illustrate here 2 possible configurations (out of ∞ many!) for the case of $N=4$ fermions:



config. amplitude

$$f(n_1=1, n_2=1, n_3=1, n_4=1, n_{\geq 5}=0; t)$$

Here is another example:



config. amplitude

$$f(n_1=1, n_2=0, n_3=1, n_4=1, n_5=0, n_6=1, n_{\geq 7}=0; t)$$

etc.

b) same problem in occupation # space

Hamiltonian $\hat{H} = \hat{T}^{(1)} + \hat{V}^{(1)} + \hat{V}^{(2)} + \hat{V}^{(3)} + \dots$

$\hat{T}^{(1)}$ = kin. energy $= \sum_{k,l=1}^{\infty} \langle k | -\frac{\hbar^2}{2m}\nabla^2 | l \rangle \hat{c}_k^+ \hat{c}_l$

$\hat{V}^{(1)}$ = external 1-body pot. $= \sum_{k,l=1}^{\infty} \langle k | v^{(1)} | l \rangle \hat{c}_k^+ \hat{c}_l$

$\hat{V}^{(2)}$ = 2-body int $= \frac{1}{2} \sum_{k,l,m,n=1}^{\infty} \langle kl | v^{(2)} | mn \rangle \hat{c}_k^+ \hat{c}_l^+ \hat{c}_n \hat{c}_m$

many-body state vector:

$$|\psi(t)\rangle = \sum_{n_1, n_2, \ldots, n_\infty = 0}^{(1)} f(n_1, n_2, \ldots, n_\infty; t)\, |n_1, n_2, \ldots, n_\infty\rangle$$

with

$$|n_1, n_2, \ldots, n_\infty\rangle = (\hat{c}_1^+)^{n_1} (c_2^+)^{n_2} \ldots (\hat{c}_\infty^+)^{n_\infty} |0\rangle$$

$$= \prod_{i=1}^{\infty} (\hat{c}_i^+)^{n_i} |0\rangle$$

with $n_i = 0$ or 1 (fermions) and $\sum_{i=1}^{\infty} n_i = N$

Many-body time-dep. Schrödinger eq. in occup. # space:

$$\left[\hat{H} - i\hbar \frac{\partial}{\partial t} \right] |\psi(t)\rangle = 0.$$

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ch. 7.2 | Equivalence of static N-body problem $(\hat{H} - E)|\psi\rangle = 0$ to variational principle $\delta_{(\psi)} E(\psi) = 0$

Ref: Shankar, QM, ch. 16.1
Blaizot & Ripka, p. 173-174

Theorem 1: Let $\hat{H}$ be the static Hamiltonian of an N-body system. The exact solution of the Schrödinger eq. has the form

$$\boxed{\hat{H}\,|\psi\rangle = E\,|\psi\rangle.} \qquad (*)$$

Here E and $|\psi\rangle$ may represent either the g.s. or any excited state.

The Ritz variational principle states that if we form the "energy functional" $E[\psi]$ defined as

$$\boxed{E[\psi] \overset{\text{def}}{=} \frac{\langle \psi | \hat{H} | \psi \rangle}{\langle \psi | \psi \rangle}}$$

then the variational principle

$$\boxed{\delta_{(\psi)} E[\psi] = 0} \qquad (**)$$

(where $|\psi\rangle$ is allowed to vary over the whole Hilbert space) is equivalent to the solution of the static Schrödinger eq. (*).

Proof: Rewrite $E[\psi]$ def. in the form

$$E[\psi] \langle \psi | \psi \rangle = \langle \psi | H | \psi \rangle$$

Now perform variation with respect to ψ (Morse + Feshbach, vol. 2, p. 1108):

$$\left.\begin{aligned} \underbrace{\delta E[\psi]}_{=0} \langle \psi | \psi \rangle + E \langle \delta\psi | \psi \rangle + E \langle \psi | \delta\psi \rangle \\ = \langle \delta\psi | H | \psi \rangle + \langle \psi | H | \delta\psi \rangle \end{aligned}\right\}$$

$$\Rightarrow \langle \delta\psi | H - E | \psi \rangle + \langle \psi | H - E | \delta\psi \rangle = 0 . \qquad (1)$$

We prove now that one can carry out the variations over $|\delta\psi\rangle$ and $\langle \delta\psi|$ independently. To see this, replace

$$|\delta\psi\rangle \to |i\,\delta\psi\rangle \overset{(1)}{\Rightarrow}$$

$$-i \langle \delta\psi | H - E | \psi \rangle + i \langle \psi | H - E | \delta\psi \rangle = 0 \qquad (2)$$

Multiply (1) by (i):

$$i\langle\delta\psi|H-E|\psi\rangle + i\langle\psi|H-E|\delta\psi\rangle = 0 \quad (3)$$

Add and subtract (2) and (3) yields

$$2i\langle\psi|H-E|\delta\psi\rangle = 0 \xRightarrow{|\delta\psi\rangle \text{ arbitrary}} \boxed{\langle\psi|(H-E) = 0}$$

$$-2i\langle\delta\psi|H-E|\psi\rangle = 0 \xRightarrow{\langle\delta\psi| \text{ arbitrary}} \boxed{(H-E)|\psi\rangle = 0}$$

q.e.d.

This variational eq. is exact. Its importance lies in the following fact:

Theorem 2: Let E_n and $|\psi_n\rangle$ be the exact eigenstates/eigenenergies of H:

$$H|\psi_n\rangle = E_n|\psi_n\rangle \quad \text{exact}$$

in particular: $H|\psi_0\rangle = E_0|\psi_0\rangle$ exact $(E_0 \le E_n)$

with the exact g.s. energy $E_0 = \langle\psi_0|H|\psi_0\rangle / \langle\psi_0|\psi_0\rangle$.

For any arbitrary state vector $|\phi\rangle$, one has the inequality:

$$E_0 = \frac{\langle\psi_0|H|\psi_0\rangle}{\langle\psi_0|\psi_0\rangle} \le E[\phi] \overset{\text{def}}{=} \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle}$$

- E_0: exact g.s. energy
- $|\psi_0\rangle$: exact g.s. state vector
- $|\phi\rangle$: arbitrary state vector

Proof: Expand given $|\phi\rangle$ in terms of exact eigenstates

$$|\phi\rangle = \sum_{n=0}^{\infty} a_n |\psi_n\rangle$$

($|\phi\rangle$: given, arbitrary; $|\psi_n\rangle$: exact)

$$\Rightarrow E[\phi] \overset{\text{def}}{=} \frac{\langle\phi|H|\phi\rangle}{\langle\phi|\phi\rangle} = \frac{\sum_{m,n} a_m^* a_n \underbrace{\langle\psi_m|H|\psi_n\rangle}_{=E_n \delta_{mn}}}{\sum_{m,n} a_m^* a_n \underbrace{\langle\psi_m|\psi_n\rangle}_{=\delta_{mn}}} =$$

$$= \frac{\sum_n |a_n|^2 E_n}{\sum_n |a_n|^2} \underset{\text{use } E_n \geq E_0}{\geq} \frac{\sum_n |a_n|^2 E_0}{\sum_n |a_n|^2} = \frac{E_0 \cancel{\sum_n |a_n|^2}}{\cancel{\sum_n |a_n|^2}}$$

$$= E_0 \quad \Rightarrow \underline{E[\phi] \geq E_0} \quad \text{q.e.d.}$$

Interpretation: Choose arbitrary state vector $|\phi\rangle$ and form energy functional $E[\phi]$. Then $E[\phi]$ is an upper bound for exact g.s. energy E_0.

Importance for HF theory: In HF theory, we restrict ourselves to the subspace of single Slater determinants $|\phi\rangle$. Using the Ritz variational principle $\delta_{(\phi)} E[\phi] = 0$, we obtain an approximate result (upper bound) for exact g.s. energy E_0.

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cl. 7.3 : Criterion for Slater determinants: $\rho^2 = \rho$

In static HF theory, one makes the approximation that the state vector of the ground state is a single Slater determinant. In occupation # space, a Slater determinant corresponds to the state vector (for N orbitals):

$$|\phi_0\rangle = \left(\hat{c}^+_{\lambda_1}\, \hat{c}^+_{\lambda_2} \cdots \hat{c}^+_{\lambda_N}\right)|0\rangle \qquad (1)$$

We introduce the density matrix parameters discussed in earlier chapters

$$\rho_{ij} = \langle i|\rho|j\rangle \overset{def}{=} \langle\phi_0|\hat{c}^+_j \hat{c}_i|\phi_0\rangle =$$

$$\overset{(1)}{=} \langle 0|\left(\hat{c}_{\lambda_N} \hat{c}_{\lambda_{N-1}} \cdots \hat{c}_{\lambda_2} \hat{c}_{\lambda_1}\right) \hat{c}^+_j \hat{c}_i \left(\hat{c}^+_{\lambda_1} \hat{c}^+_{\lambda_2} \cdots \hat{c}^+_{\lambda_N}\right)|0\rangle \qquad (2)$$

Using Wick's theorem for time-indep. operators, one can prove (Blaizot and Ripka, p. 177) that the operator ρ defined via eq. (2) can be written as

$$\boxed{\rho = \sum_{\mu=1}^{N} |\lambda_\mu\rangle\langle\lambda_\mu|} \qquad (3)$$

($|\lambda_\mu\rangle$: s.p. states)

i.e. the operator ρ may be regarded as a projector onto the space spanned by the N occupied s.p. states $|\lambda_\mu\rangle$.

Theorem: A necessary and sufficient condition for a completely antisymmetric state vector $|\phi_0\rangle$ to be a Slater determinant is that the single-particle density matrix elements $\rho_{ij} = \langle i|\rho|j\rangle$ satisfy

$$\boxed{\rho^2 = \rho}.$$

We prove the theorem in one direction only. Let's assume, we have a Slater determinant (1) which implies (3) that

$$\rho = \sum_{\mu=1}^{N} |\lambda_\mu\rangle\langle\lambda_\mu| .$$

Hence:

$$\rho^2 = \rho\cdot\rho = \left(\sum_{\mu=1}^{N} |\lambda_\mu\rangle\langle\lambda_\mu|\right)\left(\sum_{\nu=1}^{N} |\lambda_\nu\rangle\langle\lambda_\nu|\right) =$$

$$= \sum_{\mu,\nu=1}^{N} |\lambda_\mu\rangle \underbrace{\langle\lambda_\mu|\lambda_\nu\rangle}_{=\delta_{\mu\nu}} \langle\lambda_\nu| = \sum_{\mu=1}^{N} |\lambda_\mu\rangle\langle\lambda_\mu| = \rho .$$

q.e.d.

One can also prove the theorem in the opposite direction (Blaizot & Ripka, p. 178 and Ring & Schuck, Appendix D).

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ch. 7.4: The "Hartree potential" in atomic physics

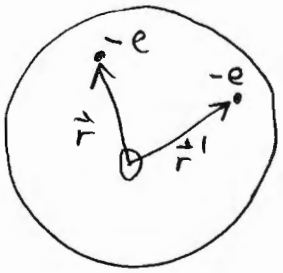
Shortly after the discovery of quantum mechanics by Heisenberg (1925) and Schrödinger (1926), the British physicist Hartree introduced in 1928 a simple model wavefunction to describe an N-electron atom. He

neglected the antisymmetry and used a simple product WF of the form

$$\Psi(x_1, x_2, \ldots, x_N) = \varphi_1(x_1)\,\varphi_2(x_2)\cdots\varphi_N(x_N).$$

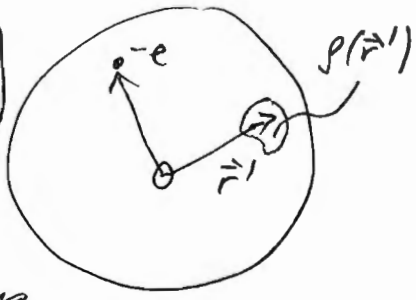
Using a variational principle for the s.p. WF's $\varphi_i(x_i)$, he was able to derive from the given electron-electron interaction (2-body potential)

$$v^{(2)}(\vec{r}, \vec{r}\,') = \frac{(-e)(-e)}{|\vec{r} - \vec{r}\,'|}$$



a one-body "mean field" potential

$$\boxed{V_H^{(1)}(\vec{r}) = \int d^3r'\, \rho(\vec{r}\,')\, v^{(2)}(\vec{r}, \vec{r}\,')}$$



where $\rho(\vec{r}\,')$ is the quantum mechanical number density distribution of the electrons, i.e. the sum of the squares of the occupied s.p. WF's:

$$\boxed{\rho(\vec{r}\,') = \sum_{\sigma=\uparrow\downarrow} \sum_{\alpha=1}^{N} |\varphi_\alpha(\vec{r}\,', \sigma)|^2}$$

This one-body potential is named in his honor the "Hartree potential".

In 1930, the Russian physicist Fock generalized Hartree's method for atoms by including the anti-symmetry. In this way, he derived an additional "Fock" exchange potential.

d.7.5 Derivation of HF-equations from Ritz variational principle (occupation # space)

Ref: Blaizot & Ripka, p. 177-180

We consider a system of N fermions (at zero temperature $T=0$) described by the Hamiltonian

$$\hat{H} = \hat{T}^{(1)} + \hat{V}^{(2)} \qquad (1)$$

where $\hat{T}^{(1)}$ is the full 1-body operator (in the N-electron atom case $\hat{T}^{(1)}$ = kin. energy + electron-nucleus interaction).

In the HF theory, one assumes that the ground state is a single Slater determinant

$$\phi_0(x_1, \ldots, x_N) = \frac{1}{\sqrt{N!}} \begin{vmatrix} \varphi_1(x_1) & \cdots & \varphi_1(x_N) \\ \vdots & & \vdots \\ \varphi_N(x_1) & \cdots & \varphi_N(x_N) \end{vmatrix} \qquad (2)$$

composed of N orthonormal s.p. wave functions

$$\left.\begin{aligned} &\varphi_i(x) = \langle x | i \rangle \qquad i = 1, \ldots, N \\ &\langle i | j \rangle = \delta_{ij} \qquad \text{orthonormality} \\ &\sum_{i=1}^{\infty} |i\rangle\langle i| = 1 \qquad \text{completeness} \end{aligned}\right\} \qquad (3)$$

In occupation # space, the Slater determinant corresponds to the state vector

$$|\phi_0\rangle = \left(\hat{c}_1^+ \hat{c}_2^+ \cdots \hat{c}_N^+\right)|0\rangle. \qquad (4)$$

Important note: We do not specify the s.p. basis. Rather, the basis WF's $\varphi_i(x)$ will be determined self-consistently from the HF theory via a variational principle!

First we calculate the g.s. energy in the state $|\phi_0\rangle$:

$$E_0 = \langle\phi_0|\hat{H}|\phi_0\rangle = \langle\phi_0|\hat{T}^{(1)} + \hat{V}^{(2)}|\phi_0\rangle =$$

$$= \sum_{k,l=1}^{\infty} \langle k|t|l\rangle \underbrace{\langle\phi_0|\hat{c}_k^+ \hat{c}_l|\phi_0\rangle}_{= \rho_{lk} \text{ (ch. 2, p. 31)}}$$

$$+ \frac{1}{2} \sum_{k,l,m,n=1}^{\infty} \langle kl|v|\underbrace{mn}\rangle \underbrace{\langle\phi_0|\hat{c}_k^+ \hat{c}_l^+ \hat{c}_n \hat{c}_m|\phi_0\rangle}_{\text{note sequence!}}$$

$$= \text{Wick's theorem (ch. 4, p. 14)}$$

$$= \rho_{nl}\cdot\rho_{mk} - \rho_{nk}\cdot\rho_{ml}$$

We see that the g.s. energy depends on the density parameters ρ_{nl}:

$$E_0(\underline{\underline{\rho}}) = \sum_{k,l} \langle k|t|l\rangle \rho_{lk} + \frac{1}{2} \sum_{k,l,m,n} \langle kl|v|mn\rangle \rho_{mk}\cdot\rho_{nl}$$

$$- \frac{1}{2} \sum_{klmn} \langle kl|v|mn\rangle \rho_{nk}\cdot\rho_{ml}.$$

If we relabel in the last term the dummy indices

$$n \leftrightarrow m,$$

we can combine the last two terms into one:

$$E_0(\rho) = \sum_{k,l=1}^{\infty} \langle k|t|l\rangle \rho_{lk} + \frac{1}{2} \sum_{k,l,m,n=1}^{\infty} \underbrace{\langle kl|v|mn - nm\rangle}_{\stackrel{\text{def}}{=} \langle kl|\bar{v}|mn\rangle} \rho_{mk}\rho_{nl} \qquad (5)$$

The quantity $\langle kl|\bar{v}|mn\rangle$ is an antisymmetrized 2-body matrix element.

Since the g.s. energy depends on the density parameters ρ_{ij}, it seems logical to try a variational principle in the form

$$\delta|_{\rho_{ij}} E_0(\rho) = 0.$$

However, in this form, we have not yet specified that the variation is to be carried out in the space of single Slater determinants which is given by the condition

$$\rho^2 = \rho. \qquad (6)$$

We can couple in this condition via a Lagrange multiplier matrix Λ; the correct Ritz variational principle is:

$$\delta|_{\rho_{ij}} \left[E_0(\rho) - \mathrm{tr}\left\{ \Lambda \cdot \underbrace{(\rho^2 - \rho)}_{\text{single Slater det.}} \right\} \right] = 0 \qquad (7)$$

($E_0(\rho)$: g.s. energy; Λ: Lagr. multiplier matrix)

Note that because ρ_{ij} is a matrix, the quantity Λ is also a matrix. In (7), "tr" is the trace of a matrix:

$$tr\{A\} \overset{def}{=} \sum_i A_{ii} . \qquad (8)$$

Let's carry out the variation of the 2nd term in eq. (7) first:

$$\delta|_\rho \left[-tr\{\Lambda\cdot(\rho\cdot\rho-\rho)\}\right] = tr\left[-\Lambda\cdot\delta\rho\cdot\rho-\Lambda\cdot\rho\cdot\delta\rho+\Lambda\cdot\delta\rho\right] \qquad (9a)$$

Using the property of traces

$$tr\{ABC\} = tr[CAB] \Rightarrow tr[-\Lambda\cdot\delta\rho\cdot\rho] = tr[-\rho\cdot\Lambda\cdot\delta\rho]$$

↖ cyclic permutation

we can write (9a) in the form

$$\boxed{\delta|_\rho \left[-tr\{\Lambda\cdot(\rho^2-\rho)\}\right] = tr\left[(-\rho\cdot\Lambda-\Lambda\cdot\rho+\Lambda)\cdot\delta\rho\right]} \qquad (9b)$$

The goal is now to also write the 1st term in (7) in the form of a trace:

$$\boxed{\delta|_\rho[E_0(\rho)]} = \sum_{i,j} \underbrace{\frac{\partial E_0}{\partial \rho_{ji}}}_{\overset{def}{=} h_{ij}} \delta\rho_{ji} = \sum_{i,j} h_{ij}\,\delta\rho_{ji} =$$

$$= \sum_i \left(\sum_j h_{ij}\,\delta\rho_{ji}\right) = \sum_i (h\cdot\delta\rho)_{ii} = \boxed{tr[h\cdot\delta\rho]} \qquad (10)$$

Note the placement of indices in the definition of

$$\boxed{h_{ij} \overset{def}{=} \frac{\partial E_0}{\partial \rho_{ji}}} \qquad (11)$$

The s.p. Hamiltonian h_{ij} will turn out to be the "Hartree-Fock" mean field Hamiltonian

$$h_{ij} \equiv h_{ij}^{HF} = \langle i|h|j\rangle = \frac{\partial E_0(\rho)}{\partial \rho_{ji}} = \underline{\text{homework!}} =$$
$$= \langle i|t|j\rangle + \sum_{k,l=1}^{\infty} \langle ik|\bar{\bar{v}}^{(2)}|jl\rangle \rho_{lk}. \qquad (12)$$

Note that in the 2nd term of (12) one sums over k and l, so that this matrix element may be regarded as a s.p. matrix element of the form

$$\langle i|V^{(1)}|j\rangle \overset{\text{def}}{=} \sum_{k,l=1}^{\infty} \langle ik|\bar{\bar{v}}^{(2)}|jl\rangle \rho_{lk}. \qquad (13)$$

$\langle i|V^{(1)}|j\rangle$: HF one-body "mean field"

$\bar{\bar{v}}^{(2)}$: given two-body interaction

Inserting (10) and (9b) into the variational principle equation (7) results in

$$\mathrm{tr}\left[\underbrace{(h - \rho\Lambda - \Lambda\rho + \Lambda)}_{\overset{!}{=}0} \cdot \underbrace{\delta\rho}_{\uparrow \text{arbitrary variation}} \right] = 0 \qquad (14)$$

So the var. principle results in

$$(\ldots) = 0 \Rightarrow \boxed{h = \rho\Lambda + \Lambda\rho - \Lambda}. \qquad (15)$$

Let us now evaluate the commutator of h and ρ:

$$[h,\rho] = h\rho - \rho h \overset{(115)}{=} (\rho\Lambda\rho + \Lambda\rho^2 - \Lambda\rho) - \rho^2\Lambda - \rho\Lambda\rho + \rho\Lambda$$

We now impose the condition for Slater determinant, $\rho^2 = \rho$:

$$[h,\rho] = \Lambda\rho - \Lambda\rho - \rho\Lambda + \rho\Lambda = 0$$

resulting in the

$$\boxed{\text{"HF-equations"}: \quad [h,\rho] = 0} \qquad (16)$$

What does this condition mean? It implies that there exists a common eigenbasis $|\alpha\rangle$ which diagonalizes both the s.p. mean-field Hamiltonian h and the density matrix parameter ρ:

$$[h,\rho] = 0 \quad \Rightarrow \quad \begin{aligned} h|\alpha\rangle &= \varepsilon_\alpha |\alpha\rangle \\ \rho|\alpha\rangle &= n_\alpha |\alpha\rangle \end{aligned} \qquad (17a)$$

Alternatively, projecting from the left with $\langle\beta|$, we get

$$\boxed{\begin{aligned} h_{\beta\alpha} &= \langle\beta|h|\alpha\rangle = \varepsilon_\alpha \langle\beta|\alpha\rangle = \varepsilon_\alpha \delta_{\alpha\beta} \\ \rho_{\beta\alpha} &= \langle\beta|\rho|\alpha\rangle = n_\alpha \langle\beta|\alpha\rangle = n_\alpha \delta_{\alpha\beta} \end{aligned}} \qquad (17b)$$

Let's examine the 2nd eigenvalue eqn. first. One easily shows that

$$\boxed{\begin{aligned} n_\alpha &= 0 \text{ or } 1 \\ \mathrm{tr}(\rho) &= N \end{aligned}} \qquad (17c)$$

Proof: (Blaizot & Ripka, p. 177–178)

a) $\rho^2|\alpha\rangle = \rho(\rho|\alpha\rangle) \overset{(17a)}{=\!=} \rho(n_\alpha|\alpha\rangle) = n_\alpha(\rho|\alpha\rangle) \overset{(17a)}{=\!=}$

$= n_\alpha^2|\alpha\rangle$

$\Rightarrow n_\alpha^2|\alpha\rangle = \rho^2|\alpha\rangle \overset{\rho^2=\rho}{=\!=} \rho|\alpha\rangle = n_\alpha|\alpha\rangle$

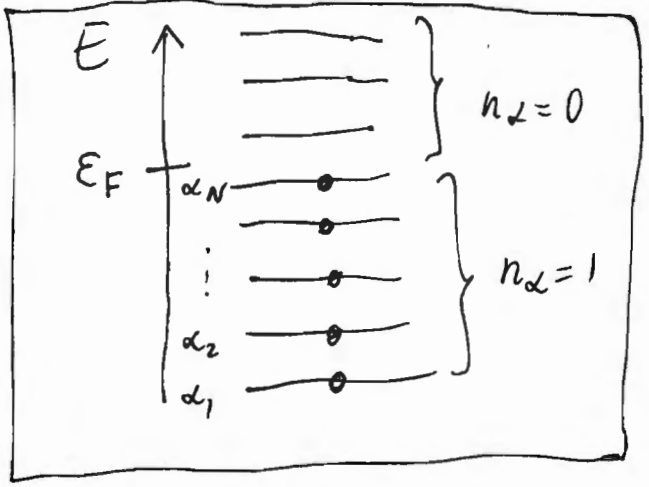
$\Rightarrow (n_\alpha^2 - n_\alpha)|\alpha\rangle = 0 \Rightarrow n_\alpha(n_\alpha - 1) = 0 \Rightarrow n_\alpha = 0 \text{ or } 1$

b) $\mathrm{tr}(\rho) = \sum_{\alpha=1}^{\infty} \rho_{\alpha\alpha} = \sum_{\alpha=1}^{\infty} \langle\alpha|\underbrace{\rho|\alpha\rangle}_{=n_\alpha|\alpha\rangle} = \sum_{\alpha=1}^{\infty} n_\alpha \underbrace{\langle\alpha|\alpha\rangle}_{=1} =$

$= \sum_{\alpha=1}^{\infty} n_\alpha = \sum_{\alpha=1}^{\infty} \theta(\varepsilon_F - \varepsilon_\alpha) = \sum_{\alpha=1}^{N} 1 = N,$

($n_\alpha \downarrow 0 \text{ or } 1$)

where we have now ordered the N s.p. WF's which are occupied ($n_\alpha = 1$) according to their energy; this defines the HF Slater determinant in occupation # space



$$|\phi_0^{HF}\rangle = \left(\hat{c}_{\alpha_1}^{+}\, \hat{c}_{\alpha_2}^{+} \dots \hat{c}_{\alpha_N}^{+}\right)|0\rangle \qquad (17d)$$

and the above considerations show that

$$n_\alpha = \theta(\varepsilon_F - \varepsilon_\alpha); \quad \rho_{\beta\alpha} = n_\alpha \delta_{\alpha\beta} \qquad (17e)$$

This is the same relation we found in earlier chapters for the non-interacting g.s.

Insert (17e) into eq. (15) for g.s. energy

$$E_0^{HF}(\rho) = \sum_{k,l=1}^{\infty} \langle k|t|l\rangle\, \theta(\varepsilon_F - \varepsilon_k)\, \delta_{lk}$$

$$+ \frac{1}{2} \sum_{k,l,m,n=1}^{\infty} \langle kl|\bar{v}|mn\rangle\, \theta(\varepsilon_F - \varepsilon_k)\, \theta(\varepsilon_F - \varepsilon_l)\, \delta_{mk}\, \delta_{nl}$$

$\Rightarrow$

$$E_0^{HF}(\rho) = \sum_{k=1}^{N} \langle k|t|k\rangle + \frac{1}{2} \sum_{k,l=1}^{N} \underbrace{\langle kl|\bar{v}|kl\rangle}_{\stackrel{def}{=} \langle kl|v|kl-lk\rangle}$$

HF ground state energy (18)

Similarly, we find from inserting (17e) into mean-field eq. (17b), using the expression (12):

$$\varepsilon_\alpha \delta_{\alpha\beta} = h_{\beta\alpha} = \langle\beta|h^{HF}|\alpha\rangle \overset{(12)}{=} \langle\beta|t|\alpha\rangle$$

$$+ \sum_{\mu,\nu=1}^{\infty} \langle\beta\mu|\bar{v}|\alpha\nu\rangle\, \rho_{\nu\mu}$$

$$= \theta(\varepsilon_F - \varepsilon_\mu)\delta_{\nu\mu}$$

resulting in the

HF-eqns in "energy representation"

$$h^{HF}_{\beta\alpha} = \langle\beta|h^{HF}|\alpha\rangle = \langle\beta|t|\alpha\rangle + \sum_{\mu=1}^{N} \underbrace{\langle\beta\mu|\bar{v}|\alpha\mu\rangle}_{\stackrel{def}{=} \langle\beta\mu|v|\alpha\mu-\mu\alpha\rangle}$$

$$= \varepsilon_\alpha \delta_{\alpha\beta}. \qquad (19)$$

The HF s.p. matrix elements, in turn, define the HF s.p. Hamiltonian in occupation # space:

$$\hat{H}^{(1)}_{HF} = \sum_{\alpha,\beta=1}^{\infty} \langle \beta | h^{HF} | \alpha \rangle \hat{c}^{+}_{\beta} \hat{c}_{\alpha} =$$

$$= \sum_{\alpha,\beta=1}^{\infty} \varepsilon_{\alpha} \delta_{\alpha\beta} \hat{c}^{+}_{\beta} \hat{c}_{\alpha} = \sum_{\alpha=1}^{\infty} \varepsilon_{\alpha} \underbrace{\hat{c}^{+}_{\alpha} \hat{c}_{\alpha}}_{=\hat{n}_{\alpha}} , \text{ i.e.}$$

$$\boxed{\hat{H}^{(1)}_{HF} = \sum_{\alpha,\beta=1}^{\infty} \langle \beta | h^{HF} | \alpha \rangle \hat{c}^{+}_{\beta} \hat{c}_{\alpha} = \sum_{\alpha=1}^{\infty} \varepsilon_{\alpha} \hat{n}_{\alpha}} \quad (20)$$

(h^{HF}: HF s.p. Hamiltonian; ε_{α}: HF s.p. energies)

ch.7.6: HF equations in coordinate space

We start from the eqns (19)

$$\langle \beta | h | \alpha \rangle = \langle \beta | t | \alpha \rangle + \sum_{\mu=1}^{N} \langle \beta\mu | v | \alpha\mu - \mu\alpha \rangle \quad (1)$$

and we insert the completeness relations for (spin + space) in the form

$$\int dx \, |x\rangle\langle x| = 1 \Rightarrow \boxed{\int d^3r \sum_{\sigma=\pm\frac{1}{2}} |\vec{r}\sigma\rangle\langle\vec{r}\sigma| = 1} \quad (2)$$

($|x\rangle = |\vec{r}\sigma\rangle$)

$\langle \beta | h | \alpha \rangle =$

$$\Rightarrow \langle \beta | \int d^3r \sum_{\sigma} |\vec{r}\sigma\rangle\langle r\sigma| \, h \, | \int d^3r' \sum_{\sigma'} |\vec{r}'\sigma'\rangle\langle\vec{r}'\sigma'| \alpha \rangle =$$

Continued on next page!

$$= \langle \beta | \int d^3r \sum_\sigma |\vec{r}\sigma\rangle\langle\vec{r}\sigma| t | \int d^3r' \sum_{\sigma'} |\vec{r}'\sigma'\rangle\langle\vec{r}'\sigma'|\alpha\rangle +$$

$$+ \sum_{\mu=1}^{N} \langle \beta\mu | \int d^3r \sum_\sigma \int d^3r_2 \sum_{\sigma_2} |\vec{r}\sigma, \vec{r}_2\sigma_2\rangle\langle\vec{r}\sigma, \vec{r}_2\sigma_2| v^{(2)} |$$

$$\times \int d^3r' \sum_{\sigma'} \int d^3r_2' \sum_{\sigma_2'} |\vec{r}'\sigma', \vec{r}_2'\sigma_2'\rangle\langle\vec{r}'\sigma', \vec{r}_2'\sigma_2'| \alpha\mu - \mu\alpha\rangle \quad (20)$$

Rewrite in usual notation with WF's:

$$\int d^3r \int d^3r' \sum_{\sigma\sigma'} \varphi_\beta^*(\vec{r}\sigma)\, h(\vec{r}\sigma, \vec{r}'\sigma')\, \varphi_\alpha(\vec{r}'\sigma') =$$

$$= \int d^3r \int d^3r' \sum_{\sigma\sigma'} \varphi_\beta^*(\vec{r}\sigma)\, t(\vec{r}\sigma, \vec{r}'\sigma')\, \varphi_\alpha(\vec{r}'\sigma') +$$

$$+ \int d^3r \int d^3r' \sum_{\sigma\sigma'} \int d^3r_2 \int d^3r_2' \sum_{\sigma_2\sigma_2'} \varphi_\beta^*(\vec{r}\sigma) \sum_{\mu=1}^{N} \varphi_\mu^*(\vec{r}_2\sigma_2)$$

$$\cdot v^{(2)}(\vec{r}\sigma, \vec{r}_2\sigma_2; \vec{r}'\sigma', \vec{r}_2'\sigma_2') \left[\varphi_\alpha(\vec{r}'\sigma')\varphi_\mu(\vec{r}_2'\sigma_2') - \right.$$

$$\left. - \varphi_\mu(\vec{r}'\sigma')\varphi_\alpha(\vec{r}_2'\sigma_2') \right]$$

from which we may conclude (leave out the underlined projection $\langle$ on the left sides):

$$h(\vec{r}\sigma, \vec{r}'\sigma')\, \varphi_\alpha(\vec{r}'\sigma') = t(\vec{r}\sigma, \vec{r}'\sigma')\, \varphi_\alpha(\vec{r}'\sigma') +$$

$$+ \sum_{\mu=1}^{N} \int d^3r_2 \int d^3r_2' \sum_{\sigma_2\sigma_2'} \varphi_\mu^*(\vec{r}_2\sigma_2)\, v^{(2)}(\vec{r}\sigma, \vec{r}_2\sigma_2; \vec{r}'\sigma', \vec{r}_2'\sigma_2')$$

$$\cdot \left[\varphi_\alpha(\vec{r}'\sigma')\varphi_\mu(\vec{r}_2'\sigma_2') - \varphi_\mu(\vec{r}'\sigma')\varphi_\alpha(\vec{r}_2'\sigma_2') \right] \quad (3)$$

Introduce the "coordinate-spin exchange operator"

$$P_{ex}\left[(\vec{r}'\sigma') \leftrightarrow (\vec{r}_2'\sigma_2')\right]$$

we can write the last expression in the shorthand form (again leave out the underlined terms, so this becomes an "operator equation" for the integral kernel h):

$$h(\vec{r}\sigma, \vec{r}'\sigma') = t(\vec{r}\sigma, \vec{r}'\sigma') + \sum_{\mu=1}^{N} \int d^3r_2 \int d^3r_2' \sum_{\sigma_2\sigma_2'} \varphi_\mu^*(\vec{r}_2\sigma_2)$$
$$v^{(2)}(\vec{r}\sigma, \vec{r}_2\sigma_2; \vec{r}'\sigma', \vec{r}_2'\sigma_2') \left[1 - P_{ex}\left[(\vec{r}'\sigma') \leftrightarrow (\vec{r}_2'\sigma_2')\right]\right] \varphi_\mu(\vec{r}_2'\sigma_2') \quad (4)$$

This is the most general expression for the mean-field kernel (non-local one-body field, in general!).

Let us now assume that the one- and two-body operators on the RHS are both local, i.e. see e.g. Shankar, QM, p.64

$$t(\vec{r}\sigma, \vec{r}'\sigma') \equiv \langle \vec{r}\sigma | t | \vec{r}'\sigma' \rangle = \delta(\vec{r}' - \vec{r})\, \delta_{\sigma'\sigma} \left[-\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V^{(1)}(\vec{r}) \right]$$

where

$$V^{(1)}(\vec{r}) = -\frac{Ze^2}{r}, \quad \text{atomic physics}$$
$$V^{(1)}(\vec{r}) = 0, \quad \text{nuclear physics} \quad (5)$$

and

$$v^{(2)}(\vec{r}\sigma, \vec{r}_2\sigma_2; \vec{r}'\sigma', \vec{r}_2'\sigma_2') \overset{\text{local!}}{=} \delta(\vec{r} - \vec{r}')\, \delta_{\sigma\sigma'}\, \delta(\vec{r}_2 - \vec{r}_2')\, \delta_{\sigma_2\sigma_2'} \cdot v^{(2)}(\vec{r}\sigma, \vec{r}_2\sigma_2) \quad (6)$$

where in the atomic case we have simply

$$v^{(2)}(\vec{r}\sigma, \vec{r}_2\sigma_2) \equiv v^{(2)}(\vec{r}, \vec{r}_2) = e^2/|\vec{r} - \vec{r}_2|.$$

Inserting eqns (6), (5) and (4) into eq. (2)

$$\int d^3r' \sum_{\sigma'} h(\vec{r}\sigma, \vec{r}'\sigma') \varphi_\alpha(\vec{r}'\sigma') = \varepsilon_\alpha \varphi_\alpha(\vec{r}\sigma)$$

results in

$$\int d^3r' \sum_{\sigma'} \delta(\vec{r}'-\vec{r}) \delta_{\sigma'\sigma} \left[-\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V^{(1)}(\vec{r}) \right] \varphi_\alpha(\vec{r}'\sigma') +$$

$$+ \int d^3r' \sum_{\sigma'} \sum_{\mu=1}^{N} \int d^3r_2 \int d^3r_2' \sum_{\sigma_2} \sum_{\sigma_2'} \varphi_\mu^*(\vec{r}_2\sigma_2)$$

$$\delta(\vec{r}'-\vec{r}) \delta_{\sigma'\sigma} \delta(\vec{r}_2'-\vec{r}_2) \delta_{\sigma_2'\sigma_2} v^{(2)}(\vec{r}\sigma, \vec{r}_2\sigma_2) \cdot$$

$$\cdot \left[1 - P_{ex}[(\vec{r}'\sigma') \leftrightarrow (\vec{r}_2'\sigma_2')] \right] \varphi_\mu(\vec{r}_2'\sigma_2') \varphi_\alpha(\vec{r}'\sigma') =$$

$$= \varepsilon_\alpha \varphi_\alpha(\vec{r}\sigma)$$

or, after simplifying the integrals over δ-factors and Σ's over δ's:

$$\left[-\frac{\hbar^2}{2m} \nabla_{\vec{r}}^2 + V^{(1)}(\vec{r}) \right] \varphi_\alpha(\vec{r}\sigma) + \sum_{\mu=1}^{N} \int d^3r_2 \sum_{\sigma_2} \varphi_\mu^*(\vec{r}_2\sigma_2) \cdot$$

$$\cdot v^{(2)}(\vec{r}\sigma, \vec{r}_2\sigma_2) \left[\varphi_\mu(\vec{r}_2\sigma_2) \varphi_\alpha(\vec{r}\sigma) - \varphi_\mu(\vec{r}\sigma) \varphi_\alpha(\vec{r}_2\sigma_2) \right] =$$

$$= \varepsilon_\alpha \varphi_\alpha(\vec{r}\sigma)$$

HF eqns for local 1-body and 2-body interactions $t^{(1)}$ and $v^{(2)}$

In general, one cannot simplify this any further. (7)

However, if $v^{(2)}(\vec{r}\sigma, \vec{r}_2\sigma_2)$ does not contain any derivative operators, then the order of the WF's is arbitrary, and we can combine them to yield densities and density matrices:

Use def. of density (for given spin projection σ_2):

$$\boxed{\rho(\vec{r}_2,\sigma_2) = \sum_{\mu=1}^{N} |\varphi_\mu(\vec{r}_2,\sigma_2)|^2} \quad (8a)$$

and def. of density matrix

$$\boxed{\rho(\vec{r},\sigma;\vec{r}_2,\sigma_2) = \sum_{\mu=1}^{N} \varphi_\mu^*(\vec{r}_2,\sigma_2)\,\varphi_\mu(\vec{r},\sigma)} \quad (8b)$$

and define the (local) "Hartree" mean-field potential

$$\boxed{V_H(\vec{r},\sigma) = \int d^3r_2 \sum_{\sigma_2=\pm\frac{1}{2}} \rho(\vec{r}_2,\sigma_2)\, v^{(2)}(\vec{r}\sigma,\vec{r}_2\sigma_2)} \quad (8c)$$

1-body mean field — density — given 2-body int.

and define the (non-local) exchange potential (= "Fock potential")

$$\boxed{V_F(\vec{r}\sigma,\vec{r}_2\sigma_2) = -\rho(\vec{r}\sigma,\vec{r}_2\sigma_2)\, v^{(2)}(\vec{r}\sigma,\vec{r}_2\sigma_2)} \quad (8d)$$

Fock exchange pot. — density matrix — given 2-body int.

we can write eq. (7) in the form

$$\boxed{\left[-\frac{\hbar^2}{2m}\nabla^2 + V^{(1)}(\vec{r})\right]\varphi_\alpha(\vec{r},\sigma) + V_H(\vec{r},\sigma)\,\varphi_\alpha(\vec{r},\sigma) + \int d^3r_2 \sum_{\sigma_2} V_F(\vec{r}\sigma,\vec{r}_2\sigma_2)\,\varphi_\alpha(\vec{r}_2,\sigma_2) = \varepsilon_\alpha\,\varphi_\alpha(\vec{r},\sigma)} \quad (8e)$$

where $\alpha = 1,\dots,N$ (occupied s.p. states)
and $V^{(1)}(\vec{r}) = -Ze^2/r$ (atoms) and $V^{(1)}(\vec{r}) \equiv 0$ (nuclei)

The eqns (8c) are the Hartree-Fock equations under the simplifying assumptions of

a) local one- and two-body operators (see p. 21)

b) 2-body int. contains no derivative operators (otherwise need to use HF-eqns in eq. (7)).

Comments on structure of HF eqns in coordinate space

1) If we leave out the Fock term for a moment, then the HF eqns look very much like N Schrödinger equations for the s.p. WF's $\varphi_\alpha(\vec{r},\sigma)$ with $\alpha = 1, \ldots, N$. However, this simplicity is deceptive: the 1-body Hartree potential $V_H(\vec{r},\sigma)$ involves an integral over the 2-body int. and the g.s. density of the system, eq. (8c), and the density (8a) involves a sum over all occupied s.p. WF's.

2) This gives rise to a "self-consistency problem": to solve HF-eqn for given s.p. WF $\varphi_\alpha(\vec{r},\sigma)$, we need to know all s.p. WF's.

↓ requires iterative solution (see below)

3) The Fock exchange potential complicates the situation further because it involves an integral over the density matrix and the given 2-body interaction.

4) Nevertheless, the static HF equations are much simpler than the original N-body Schrödinger eq., and we have achieved our main goal:

> The Hartree and Fock "mean field" potentials take the 2-body interaction $v^{(2)}(\vec{r}_1\sigma_1, \vec{r}_2\sigma_2)$ into account "on average". In particular, the Hartree term $V_H(\vec{r},\sigma)$ is a 1-body mean field.

Comments on numerical, iterative solution

1) For atoms or nuclei, use simple shell model WF's in zeroth-order approximation, i.e.

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + V^{(1)}_{\text{s.m.}}(\vec{r})\right]\varphi^{(0)}_\alpha(\vec{r},\sigma) = \varepsilon^{(0)}_\alpha \varphi^{(0)}_\alpha(\vec{r},\sigma) \qquad (9a)$$

For atom, use electron-nucleus Coulomb potential

$$V^{(1)}_{\text{s.m.}}(\vec{r}) = -\frac{Ze^2}{|\vec{r}|} \qquad (9b)$$

and in nuclear case, use phenomenological 3-D harmonic oscillator potential

$$V^{(1)}_{\text{s.m.}}(\vec{r}) = \frac{1}{2}m\omega^2\vec{r}^{\,2}. \qquad (9c)$$

The WF's $\varphi^{(0)}_\alpha(\vec{r},\sigma)$ can be obtained analytically (see e.g. Shankar, QM), and from these we can compute the density / density matrix in zeroth-order

$$\rho^{(0)}(\vec{r}_2,\sigma_2) = \sum_{\mu=1}^{N} |\varphi_\mu^{(0)}(\vec{r}_2,\sigma_2)|^2 \quad . \qquad (9d)$$

↑ shell-model WF's.

Similar expression for density matrix $\rho^{(0)}(\vec{r},\sigma;\vec{r}_2\sigma_2)$.

(2) Solve HF eqns (8e) numerically with density / density matrix from shell model, $\rho^{(0)}$. This yields new S.p. WF's in 1st-order

$$\varphi_\alpha^{(1)}(\vec{r},\sigma).$$

(3) From $\varphi_\alpha^{(1)}(\vec{r},\sigma)$ obtain new density / density matrix $\rho^{(1)}$ in 1st-order. Solve HF equations (8e) with $\rho^{(1)}$ and obtain new s.p. WF's in 2nd-order

$$\varphi_\alpha^{(2)}(\vec{r},\sigma).$$

(4) Keep iterating n times. Convergence is obviously achieved if the s.p. energies $\varepsilon_\alpha^{(n)}$ and WF's $\varphi_\alpha^{(n)}$ no longer change. One typically uses the convergence criterion

$$\left| \frac{\varepsilon_\alpha^{(n+1)} - \varepsilon_\alpha^{(n)}}{\varepsilon_\alpha^{(n)}} \right| < \delta \qquad (9e)$$

where δ might be of order $\delta \approx 10^{-8}$. In practice, this might require several hundred iterations.

The solution of HF-eqns predicts

1) s.p. energies ε_α

2) s.p. WF's $\varphi_\alpha(\vec{r},\sigma)$ → calculate ground state density $\rho(\vec{r},\sigma)$. → mean square radius $\langle r^2 \rangle$.

These quantities can be compared to exp. data.

3) One can use WF's $\varphi_\alpha(\vec{r},\sigma)$ to calculate the ground state binding energy E_0^{HF}. We will now show that E_0^{HF} is a functional of various densities.

The energy density functional predicted by HF method

Earlier, we have computed the g.s. energy (see notes p.18)

$$E_0^{HF} = \sum_{\alpha=1}^{N} \langle \alpha | t | \alpha \rangle + \frac{1}{2} \sum_{\alpha,\beta=1}^{N} \langle \alpha\beta | v^{(2)} | \alpha\beta - \beta\alpha \rangle .$$

Using the same techniques as in derivation of HF-eqns in coordinate space, i.e. by inserting completeness relations of the form

$$\int d^3r \sum_\sigma |\vec{r}\sigma\rangle\langle\vec{r}\sigma| = 1$$

we obtain straightforwardly (for local int. $v^{(2)}$):

$$E_0^{HF} = \sum_{\alpha=1}^{N} \int d^3r \sum_\sigma \varphi_\alpha^*(\vec{r},\sigma) \left[-\frac{\hbar^2}{2m}\nabla^2 + V^{(1)}[\vec{r},\sigma] \right] \varphi_\alpha(\vec{r},\sigma)$$
$$+ \frac{1}{2} \sum_{\alpha,\beta=1}^{N} \int d^3r \int d^3r' \sum_{\sigma\sigma'} \varphi_\alpha^*(\vec{r},\sigma) \varphi_\beta^*(\vec{r}'\sigma') \ \ldots$$

continued on p. 28

$$v^{(2)}(\vec{r}\sigma, r'\sigma')\left[\varphi_\alpha(\vec{r},\sigma)\varphi_\beta(\vec{r}',\sigma') - \varphi_\beta(\vec{r},\sigma)\varphi_\alpha(\vec{r}',\sigma')\right]$$

"direct term" "exchange term"

We use partial integration to re-write the kin. energy term

$$E_{kin}^{HF} = \int d^3r \sum_\sigma \sum_{\alpha=1}^{N} \varphi_\alpha^*(\vec{r},\sigma)\left(-\frac{\hbar^2}{2m}\right)\nabla\cdot\nabla\varphi_\alpha(\vec{r},\sigma) =$$

$$= \pm \int d^3r \sum_\sigma \sum_{\alpha=1}^{N} \left(+\frac{\hbar^2}{2m}\left\{\nabla\varphi_\alpha^*(r,\sigma)\cdot\nabla\varphi_\alpha(\vec{r},\sigma)\right\}\right)$$

Note sign change from partial integration

$$\int_V u\,v'\,dx = uv\Big|_B - \int_V u'v\,dx$$

and the surface term vanishes because we integrate to ∞.

We <u>define</u> the <u>kinetic energy density</u>

$$\boxed{\tau(\vec{r}) = \sum_{\sigma=\pm\frac{1}{2}} \sum_{\alpha=1}^{N} \left|\nabla\varphi_\alpha(\vec{r},\sigma)\right|^2} \qquad (10a)$$

and obtain

$$\boxed{E_{kin} = \int d^3r\, \frac{\hbar^2}{2m}\,\tau(\vec{r})} \qquad (10b)$$

The remaining terms can be rewritten using the definition of the density $\rho(\vec{r},\sigma)$, eq. (8a), and density matrix $\rho(\vec{r},\sigma;\vec{r}'\sigma')$, eq. (8b). One finds straightforwardly:

$$E_0^{HF} = \int d^3r \; \underbrace{\mathcal{H}^{HF}\left(\tau(\vec{r}), \rho(\vec{r},\sigma), \rho(\vec{r}\sigma, \vec{r}'\sigma')\right)}_{= \text{HF energy density functional}}$$

g.s. energy

$$\mathcal{H}^{HF} = \underbrace{\frac{\hbar^2}{2m}\tau(\vec{r})}_{\text{kin. energy}} + \underbrace{\sum_{\sigma=\pm\frac{1}{2}} V^{(1)}(\vec{r},\sigma)\,\rho(\vec{r},\sigma)}_{\text{given 1-body pot.}}$$

$$+ \frac{1}{2}\int d^3r' \underbrace{\sum_{\sigma\sigma'=\pm\frac{1}{2}} v^{(2)}(\vec{r}\sigma, \vec{r}'\sigma')}_{\text{2-body term}} \Big[\underbrace{\rho(\vec{r},\sigma)\,\rho(\vec{r}',\sigma')}_{\text{"direct"}} - \underbrace{\left|\rho(\vec{r},\sigma;\vec{r}'\sigma')\right|^2}_{\text{"exchange"}} \Big] \qquad (11)$$

Specific case: N-electron atom

Here we have

electron-nucleus int.: $V^{(1)}(\vec{r},\sigma) \to V^{(1)}(r) = -\frac{Ze^2}{r}$

e^-e^- repulsion: $v^{(2)}(\vec{r}\sigma;\vec{r}'\sigma') \Longrightarrow v^{(2)}(\vec{r},\vec{r}') = \frac{e^2}{|\vec{r}-\vec{r}'|}$

Hence, the HF energy density of the atom becomes

$$\mathcal{H}^{HF}_{atom} = \frac{\hbar^2}{2m}\tau(\vec{r}) - \frac{Ze^2}{r}\underbrace{\sum_\sigma \rho(\vec{r},\sigma)}_{=\rho(\vec{r})} + \frac{1}{2}\int d^3r' \frac{e^2}{|\vec{r}-\vec{r}'|}$$

$$\Big[\underbrace{\sum_\sigma \rho(\vec{r},\sigma)}_{=\rho(\vec{r})} \underbrace{\sum_{\sigma'} \rho(\vec{r}',\sigma')}_{=\rho(\vec{r}')} - \underbrace{\sum_{\sigma\sigma'} \left|\rho(\vec{r}\sigma,\vec{r}'\sigma')\right|^2}_{=\left|\rho(\vec{r},\vec{r}')\right|^2} \Big].$$

Note: essentially the pair correlation function (ch. 6, eq. (101)).

We can recast this in the form

$$\mathcal{H}^{HF}_{atom} = \underbrace{\frac{\hbar^2}{2m}\tau(\vec{r})}_{\text{kin. energy}} - \underbrace{\frac{Ze^2}{r}\rho(\vec{r})}_{\substack{e^- \text{-nucleus} \\ \text{attraction}}} + \underbrace{V^D_{coul}}_{e^- \text{-} e^- \text{ int.}} + \underbrace{V^E_{coul}}_{e^- \text{-} e^- \text{ int.}} \qquad (12a)$$

where the "direct" part of the Coulomb energy is given by

$$V^D_{coul} = \frac{1}{2}\int d^3r'\, \rho(\vec{r})\frac{e^2}{|\vec{r}-\vec{r}'|}\rho(\vec{r}') \qquad (12b)$$

→ note: same expression as in classical E&M theory!

and the "exchange" part of the Coulomb energy is given by

$$V^E_{coul} = -\frac{1}{2}\int d^3r'\, \frac{e^2}{|\vec{r}-\vec{r}'|}\left|\rho(\vec{r},\vec{r}')\right|^2 \qquad (12c)$$

The "exchange" energy arises, of course, from the anti-symmetry of the g.s. Slater determinant!

HF calculations: computational issues

There are 2 basic computational approaches:

- basis expansion of HF wave functions
- lattice representation of HF wave functions

a) basis expansion method

Start from HF eqns in energy representation (ch. 7, p. 18):

$$\langle\beta|t|\alpha\rangle + \sum_{\mu=1}^{N}\langle\beta\mu|\bar{v}|\alpha\mu\rangle = \varepsilon_\alpha \underbrace{\delta_{\alpha\beta}}_{=\langle\beta|\alpha\rangle}$$

Project from the left with $\sum_\beta |\beta\rangle$:

$$\underbrace{\sum_\beta |\beta\rangle\langle\beta|}_{=1}\, t|\alpha\rangle + \sum_{\mu=1}^{N}\underbrace{\sum_\beta |\beta\rangle\langle\beta}_{=1}\mu|\bar{v}|\alpha\mu\rangle = \varepsilon_\alpha \underbrace{\sum_\beta |\beta\rangle\langle\beta|\alpha\rangle}_{=1}$$

$$\Rightarrow t|\alpha\rangle + \sum_{\mu=1}^{N}\langle \underbrace{\;}_{\text{empty!}}\mu|\bar{v}|\alpha\mu\rangle = \varepsilon_\alpha|\alpha\rangle$$

Project from left with $\langle i|$, where $|i\rangle$ denotes <u>given</u> basis set:

$$\langle i|t|\alpha\rangle + \sum_{\mu=1}^{N}\langle i\mu|\bar{v}|\alpha\mu\rangle = \varepsilon_\alpha\langle i|\alpha\rangle \qquad \underline{(1)}$$

Expand HF orbitals in terms of given s.p. basis (e.g. atomic / nuclear shell model):

$$|\alpha\rangle = \underbrace{\sum_{i=1}^{\infty}|i\rangle\langle i|\alpha\rangle}_{=1} = \sum_{i=1}^{\infty}\underbrace{\langle i|\alpha\rangle}_{\stackrel{\text{def}}{=} D_{i\alpha}}|i\rangle$$

Summary:

$$|\alpha\rangle = \sum_{i=1}^{\infty} D_{i\alpha} |i\rangle \qquad (2)$$

$|\alpha\rangle$: HF-orbital; $|i\rangle$: S.p. basis (given); $D_{i\alpha} \overset{\text{def}}{=} \langle i|\alpha\rangle$: expansion coefficients

Insert expansion $|\alpha\rangle = \sum_j D_{j\alpha} |j\rangle$ multiple times into (1):

$$\sum_j \langle i|t|j\rangle D_{j\alpha} + \sum_{\mu=1}^{N} \Big\langle i, \sum_k D_{k\mu}^{*} k \,\Big|\bar{v}\Big|\, \sum_j D_{j\alpha} j, \sum_l D_{l\mu} l \Big\rangle$$

$$= \varepsilon_\alpha D_{i\alpha}$$

$$\Rightarrow \sum_{j=1}^{\infty} \langle i|t|j\rangle D_{j\alpha} + \sum_{j,k,l=1}^{\infty} \langle ik|\bar{v}^{(2)}|jl\rangle \times \sum_{\mu=1}^{N} D_{k\mu}^{*} D_{l\mu} D_{j\alpha} = \varepsilon_\alpha D_{i\alpha} \qquad (3)$$

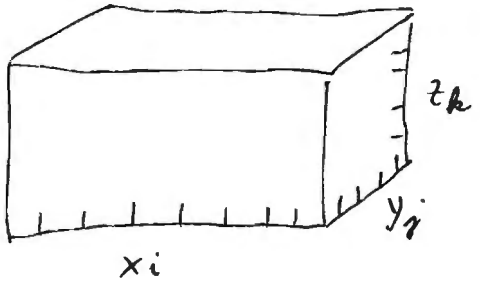
HF eqns in given basis $|i\rangle$.

agrees with Ring & Schuck, eq. (5.38)

We observe:

- The eqns (3) represent a Hermitian eigenvalue problem for the expansion coefficients $D_{i\alpha}$, which is non-linear in D ($\propto D^3$), as a result of HF approximation (the original many-body Schrödinger eq. is linear).
- To solve eqns (3), one need to calculate 1-particle matrix elements $\langle i|t|j\rangle$ and 2-particle matrix elements $\langle ik|\bar{v}^{(2)}|jl\rangle$ within the given basis $|i\rangle$ (e.g. shell model).

b) lattice representation



Continuous space $\vec{r} = (x, y, z)$

→ 3-D Cartesian lattice

(x_i, y_j, z_k) with

$$\left.\begin{aligned} i &= 1, 2, \ldots, n_x \\ j &= 1, 2, \ldots, n_y \\ k &= 1, 2, \ldots, n_z \end{aligned}\right\}$$

Consider a single HF spinor wave function

$$\varphi_\alpha(\vec{r}, \sigma) = \begin{pmatrix} \varphi_\alpha^{\uparrow}(\vec{r}) \\ \varphi_\alpha^{\downarrow}(\vec{r}) \end{pmatrix} \longrightarrow \begin{pmatrix} \varphi_\alpha^{\uparrow}(x_i, y_j, z_k) \\ \varphi_\alpha^{\downarrow}(x_i, y_j, z_k) \end{pmatrix}$$

→ the s.p. WF becomes an "array" of dimension N:

phi $(n_x, n_y, n_z, 2) \equiv$ phi (N) with

$$N = n_x \cdot n_y \cdot n_z \cdot 2$$

(2 ↑ spin up/down)

Example: Cubic lattice with $n_x = n_y = n_z =$ 30 points

$$\searrow N = 30^3 \cdot 2 = 54{,}000$$

Hence, to represent a single spinor WF on the lattice requires an array of dimension

phi(N) ; $N = 54{,}000$

Each array element is a double-precision complex number!

Representation of HF mean field Hamiltonian h on the 3-D lattice

An eigenvalue problem HF type

$$h^{HF}\,\varphi_\alpha = \varepsilon_\alpha\,\varphi_\alpha$$

requires a matrix representation of h on the lattice

$$\begin{pmatrix} & h^{HF} & \end{pmatrix}\begin{pmatrix} \varphi_\alpha \\ \downarrow \end{pmatrix} = \varepsilon_\alpha \begin{pmatrix} \varphi_\alpha \\ \downarrow \end{pmatrix}, \qquad (\alpha = 1, \ldots, N)$$

"matrix" $(N \times N)$ — "vector" $(\dim = N)$

$\rightarrow$ $\dim h^{HF} = N \times N = 54{,}000^2 = 2.9 \times 10^9$

All matrix elements = double-precision, complex #'s.

The complete diagonalization procedure requires that we store both the matrix h and all eigenvectors (W)

$$\underbrace{\begin{pmatrix} & W^+ & \end{pmatrix}}_{N\times N}\underbrace{\begin{pmatrix} & h^{HF} & \end{pmatrix}}_{N\times N}\underbrace{\begin{pmatrix} \varphi_1 & \varphi_2 & \cdots & \varphi_N \\ \downarrow & \downarrow & & \downarrow \end{pmatrix}}_{=W} = \begin{pmatrix} \varepsilon_1 & & & 0 \\ & \varepsilon_2 & & \\ & & \ddots & \\ 0 & & & \varepsilon_N \end{pmatrix}$$

The $N \times N$ matrix W containing all N eigenvectors requires the same storage as h^{HF}, i.e. N^2.

Fortunately, such a "brute-force" approach can be avoided in practice, because one is usually not interested in all eigenvalues (ε_α) and eigenvectors (φ_α). In HF theory, one

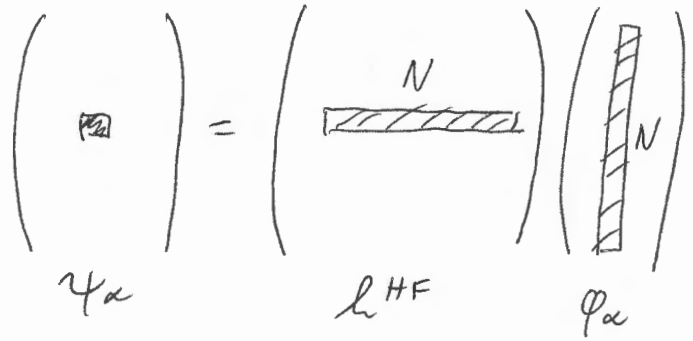
needs only the lowest N_p eigenvalues/vectors, where N_p = number of occupied s.p. states.

In this case, there are several iterative schemes available:

- "Lanczos" algorithm
- "Davidson" algorithm
- "damped gradient iteration" ← we use this one!

These methods do not require the storage of the whole $(N \times N)$ h^{HF} matrix, rather they consist of the following computational step:

$$\psi_\alpha \overset{\text{def}}{=} h^{HF} \varphi_\alpha \rightarrow$$



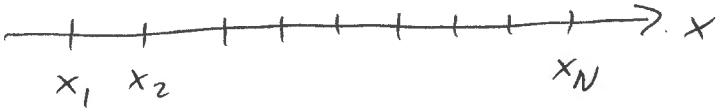
which requires that we only need to store one row of h^{HF} at a time, i.e. it requires that we store

$2N$ numbers rather than N^2 !

In our example $N = 54{,}000$; this makes a huge difference for required memory!

Representation of potentials, integrals, and derivatives on 3-D lattice

For simplicity, let us discuss a 1-D grid here:



a) a local potential $V(x)$, without any derivatives

$$V(x)\,\varphi_\alpha(x) \to V(x_i)\,\varphi_\alpha(x_i)$$

$$\Rightarrow V(x) = \begin{pmatrix} V(x_1) & & & \\ & V(x_2) & & \\ & & \ddots & \\ & & & V(x_N) \end{pmatrix}$$ diagonal matrix

b) integrals

$$\int_a^b dx\, f(x) \to \sum_{i=1}^{N} \Delta x_i\, f(x_i)$$

c) derivative operators: the main computational problem

I. simple finite-difference schemes

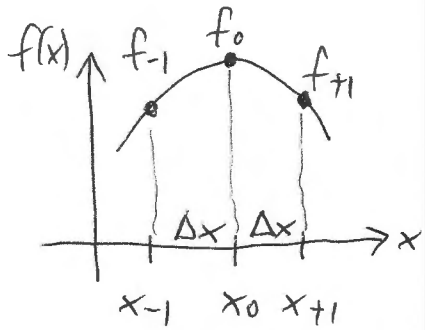
In lowest order, one derives from the Taylor expansions of

$$f(x_0+\Delta x) \quad \text{and} \quad f(x_0-\Delta x)$$

the 3-point formula

$$f'(x_0) = \frac{1}{2\Delta x}\left[-1\cdot f_{-1} + 0\cdot f_0 + 1\cdot f_{+1}\right]$$

which we can write in the form

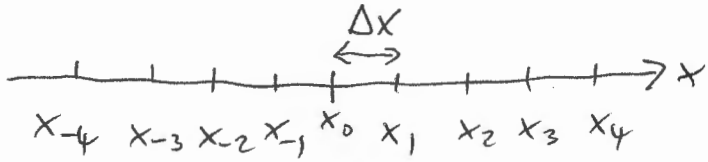


$$f'(x_0) = \sum_{i=-1}^{+1} a_i f_i \quad \text{with}$$

$$a_{-1} = \frac{1}{2\Delta x}(-1) \qquad a_0 = 0 \qquad a_{+1} = \frac{1}{2\Delta x}(+1)$$

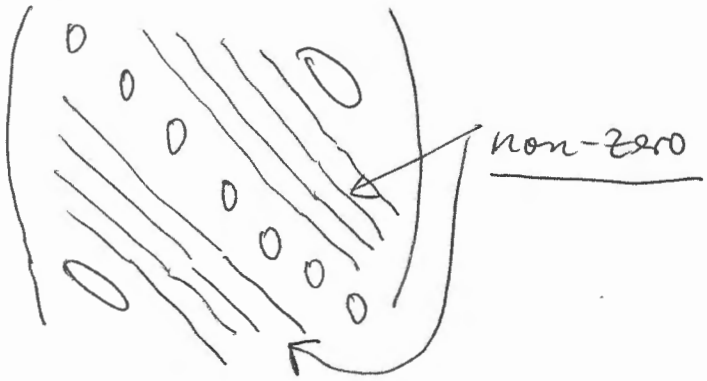
In order to achieve higher numerical accuracy, scientists typically use the 9-point formula

$$f'(x_0) = \sum_{i=-4}^{\pm 4} a_i f_i$$



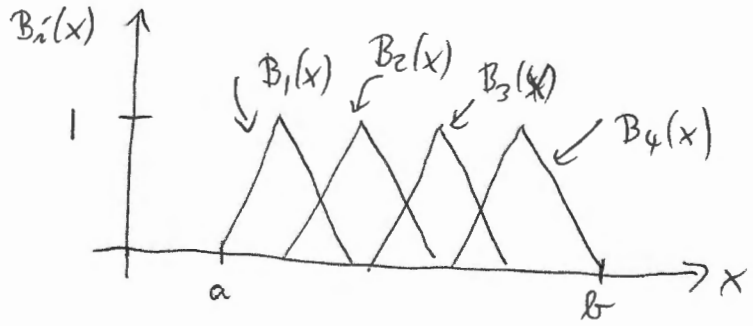
which connects the nearest 4 points to the left and right of the given point x_0. The derivative operation becomes a "relatively sparse" banded matrix:

$$\frac{d}{dx} \rightarrow$$



II. Finite elements and Basis Splines

"Finite elements" are polynomial sections of order 1, i.e. sections of straight lines:



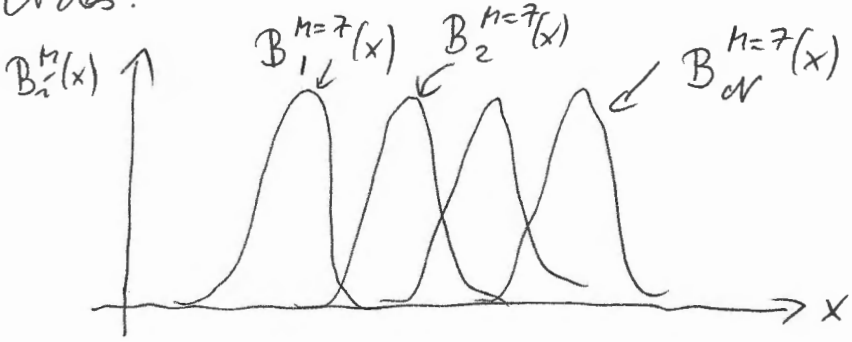
Basis-Splines (= B-Splines) are generalizations of finite elements (higher-order polynomial sections).

> B-Spline of order $M \triangleq$ polynomial sections up to order $M-1$

Special case: $M=2$ ↴ $B_i^{M=2}(x) \Leftrightarrow$ polynomials of order $M-1 = 2-1 = 1$

↴ straight line sections

In practice, we use B-Splines of order $M=7$ in HF codes:



These are polynomial sections up to order 6.

Main advantage of higher-order B-Splines: they are smoother than finite elements ↴ better accuracy of derivative operators.

Literature on B-Splines in Physics → possible term paper!

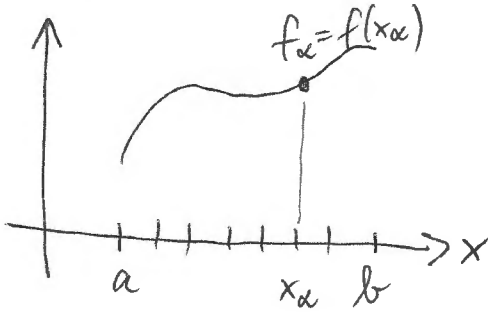
- A.S. Umar et al., J. Comp. Phys. 93 (1991) p. 426
- J.C. Wells et al., Int. J. Mod. Phys. C6 (1995) p. 143

B-Spline theory shows that one can expand a given function $f(x)$ in the finite interval $[a,b]$ by a finite superposition of B-Spline polynomial section functions $B_i^M(x)$, i.e.

$$f(x) = \sum_{i=1}^{\mathcal{N}} B_i^M(x)\, c_i$$

($B_i^M(x)$: B-Spline; c_i: expansion coefficients)

M = Spline order
N = # grid points
$\mathcal{N} = M + N - 1$



Representation of $f(x)$ on the 1-D grid points x_α ($\alpha = 1, \ldots, N$):

$$f_\alpha = f(x_\alpha) = \sum_{i=1}^{\mathcal{N}} B_i^M(x_\alpha)\, c_i$$

$$f_\alpha = \sum_{i=1}^{\mathcal{N}} B_{\alpha i}^M\, c_i$$

$B_{\alpha i}^M$ = B-Spline matrix

As explained in the computational physics papers on p. 38, one finds the following matrix representation of $\frac{d}{dx}$ in terms of B-Splines

$$\frac{d}{dx} \rightarrow D_{\alpha\beta} = \sum_{i=1}^{\mathcal{N}} \left(\frac{dB_i^M(x)}{dx} \right)_{x=x_\alpha} \cdot \left[B_i^M(x) \right]^{-1}_{x=x_\beta}$$

calculate analytically (polynomials!)

need inverse of B-Spline matrix

Features of matrix $D_{\alpha\beta}$

- Because of B^{-1}, the derivative matrix is no longer sparse, i.e. most matrix elements are $\neq 0$
  → disadvantage, as compared to finite difference method
- main advantage of B-Splins: need fewer grid points to achieve a given numerical accuracy → essential for 3-D problems (N^3).

Numerical results for static HF calculations

see Phys-365 Website, "Additional lecture materials" section

a) Powerpoint slides for atomic HF

b) " " " nuclear HF

Add. info for atomic MCHF (slide 8)

The atomic Hamiltonian commutes with the total orbital angular momentum operator and the total spin operator:

$$\vec{L} = \sum_{i=1}^{N} \vec{l}_i \qquad \vec{S} = \sum_{i=1}^{N} \vec{s}_i$$

and $[H_{atom}, \vec{L}] = 0$ and $[H_{atom}, \vec{S}] = 0$.

Mutually commuting operators:

$$H_{atom},\ \vec{L}^2,\ L_z,\ \vec{S}^2,\ S_z$$

$$H_{atom}\,\psi = E\,\psi$$
$$\vec{L}^2\,\psi = \hbar^2 L(L+1)\,\psi$$
$$L_z\,\psi = \hbar M_L\,\psi$$
$$S^2\,\psi = \hbar^2 S(S+1)\,\psi$$
$$S_z\,\psi = \hbar M_S\,\psi$$

Spectroscopic notation for total ang. momenta

$$\left({}^{2S+1}L\right)_J$$

Remarks re. slide 8:

Considered is the beryllium atom (Be, $Z=4$).

ground state electron configuration: $\boxed{1s^2\,2s^2}$

total ang. momenta: $^{2S+1}L_J \hat{=} {}^1S_0 \Rightarrow \boxed{\begin{array}{l} S=0 \\ L=0 \\ J=0 \end{array}}$ g.s.

($^1S_0$: $L=0$)

Prof. Fischer's MCHF calculations consider now the Rydberg series of excited states of the form

$\boxed{1s^2\,2s\,nd}$ with n = variable = $3, 4, 5, \ldots, 11$

total ang. momenta: $^{2S+1}L_J \hat{=} {}^3D_J$ (^3D: $L=2$)

$\boxed{\begin{array}{l} S=1 \\ L=2 \end{array} \Rightarrow J=1,2,3}$

exc. states

Density functional theory (DFT)

References:

1) P. Hohenberg and W. Kohn, Phys. Rev. B 136 (1964) 864.
2) W. Kohn and L. J. Sham, Phys. Rev. A 140 (1965) 1133
3) G. Kotliar et al., Rev. Mod. Phys. 78 (2006) 865
4) J. A. Maruhn, P.-G. Reinhard and E. Suraud, "Simple Models of Many-Fermion Systems", Springer Verlag, 2010 [pages 143-148]
5) Time-dep. density functional theory (TDDFT) example: J. A. Driscoll and K. Varga, Phys. Rev. B80 (2009) 245431

The basic ideas of (static) DFT are based on the results of atomic HF theory. Central to the theoretical development are the 2 theorems by Hohenberg and Kohn (Ref. 1) and Kohn and Sham (Ref. 2).

Most important practical applications of DFT are

- molecular physics / quantum chemistry
- condensed matter physics

Walter Kohn shared the Nobel prize in chemistry in 1998 for the impact of his work on quantum chemistry.

Review of static HF for atoms

input:

$V^{(1)}(x)$, $V^{(2)}(x,x')$

main approximation:

single Slater determinant

$$|\Psi\rangle \approx |\phi_0^{HF}\rangle$$

Output: g.s. energy functional $E_0(\rho(x), \rho(x,x'), \tau(x))$

mean field hamiltonian $h = \partial E_0 / \partial \rho$

HF eqns for orbitals $\varphi_\alpha(x)$:

$$\left[-\frac{\hbar^2}{2m_e} \nabla_{\vec{r}}^2 + V_{e^- - N}^{(1)}(\vec{r}) + V_H[\rho(\vec{r})] + V_{exch}\left(\rho(\vec{r}, \vec{r}')\right) \right] \varphi_\alpha(\vec{r}) = \varepsilon_\alpha \varphi_\alpha(\vec{r})$$

advantages:

- rigorous theory, derive everything from given $V^{(1)}(x)$, $V^{(2)}(x,x')$, in particular energy functl $E_0(\rho...)$
- all approximations clearly stated

disadvantage:

- only Pauli correlations are included (arise from totally anti-sym. WF) → see "fermion pair correlation function". Otherwise, particles move "freely" in mean field potential.

Hohenberg-Kohn Theorem (1964) for electronic systems

Hamiltonian in coord.-repr (use Born-Oppenheimer approx.):

$$H = \underbrace{\sum_{i=1}^{N} -\frac{\hbar^2}{2m_e}\nabla_i^2}_{=T_{e^-}} + \underbrace{\sum_{i=1}^{N} V^{(1)}(\vec{r}_i)}_{=V_{e^-,ion}} + \underbrace{\frac{1}{2}\sum_{i,j=1}^{N} \frac{e^2}{|\vec{r}_i - \vec{r}_j|}}_{=V_{e^-e^-}}$$

The electronic part of H is giving rise to the energy

$$E_{HK} \overset{def}{=} \langle \psi | T_{e^-} + V_{e^-e^-} | \psi \rangle .$$

The theorem starts:

a) $E_{HK} = E_{HK}[\rho(\vec{r})]$, i.e. the electronic part of the energy is a unique and universal functional of the local electron density $\rho(\vec{r})$.

b) For a given ext. field $V^{(1)}(\vec{r})$, arising from the ionic cores, the total energy is

$$E[\rho(\vec{r})] = E_{HK}[\rho(\vec{r})] + \int d^3r\, \rho(\vec{r})\, V^{(1)}(\vec{r})$$

and the exact g.s. density is obtained from variation of E with respect to ρ: $\partial E / \partial \rho = 0$.

Comments

- It is surprising that E depends only on density $\rho(\vec{r})$, but not on $\rho(\vec{r},\vec{r}')$ or on $\tau(\vec{r})$, as in HF-approximation.
- main problem: HK theorem proves existence of $E(\rho)$, but does not tell us how to derive $E(\rho)$!?

Kohn-Sham formalism (1965) for electronic systems

Based on the HK theorem, one starts with the construction of an approximate energy functional $E(\rho)$ using physical arguments (but no rigorous theory!) such as

- interacting electron gas (infinite system)
- "local density approximation" (LDA), i.e. piecewise infinite homogeneous matter.

The Kohn-Sham energy functional has the form

$$E_{KS} = \underline{\underline{T}}_{kin}(\rho) + E_{ext}(\rho) + E_H(\rho) + E_{xc}(\rho)$$

where the kinetic energy term has the same form as in HF theory, $E_{ext}(\rho)$ describes the interaction of e^- with ionic cores, E_H is the Hartree energy, and E_{xc} describes both the electron exchange energy and additional correlation effects among the electrons. From a variational principle one obtains the Kohn-Sham equations for the occupied e^- orbitals:

$$\left[-\frac{\hbar^2}{2m_e}\nabla_{\vec{r}}^2 + V_{ext}^{(1)}(\vec{r}) + V_H(\rho(\vec{r})) + V_{xc}(\vec{r}) \right] \varphi_\alpha(\vec{r}) = \varepsilon_\alpha \varphi_\alpha(\vec{r})$$

($V_{ext}^{(1)}$: electron-ions; V_H: Hartree pot.; V_{xc}: exchange + correlations)

with $V_{xc}(\vec{r}) = V_{xc}\left(\rho(\vec{r}) + \ldots + \nabla\rho + \nabla\nabla\rho\right)$

($\rho(\vec{r})$: LDA; $\nabla\rho + \nabla\nabla\rho$: higher-order corrections.)

advantages of KS formalism

- correlations are built into the E_{KS} energy functional; "pure" HF contains only "Pauli correlations".
- Works surprisingly well for molecular physics / quantum chemistry and electronic properties of condensed matter systems.

Note: possible term paper topic

- check for recent papers by Vanderbilt condensed-matter theorists (Profs. Pantelides and Varga and their research groups)!