Mean field approach - Technical details

Computational Physics

4. október 2010

Consider the Hartree (or LDA) equations of motion

$$\{H_0 + V_{\rm ext}(\mathbf{r}) + V_H(\mathbf{r})\}\psi_\alpha(\mathbf{r}) = \epsilon_\alpha \psi_\alpha(\mathbf{r})$$

$$V_H(r) = \frac{e^2}{\kappa}\int d\mathbf{r}'\ \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}$$

$$n(\mathbf{r}) = \sum_\alpha |\psi_\alpha(\mathbf{r})|^2 f(\epsilon_\alpha - \mu)$$

$$\int d\mathbf{r}'\ n(\mathbf{r}', \mu) = N, \text{ number of electrons}$$

how do we implement them?

It is possible to use a grid to solve the equations on, or finite element method.

Here we consider using a mathematical basis

We start with the Schrödinger equation that we want to solve

$$\{H_0 + V_{\text{ext}} + V_H\}\Psi_\alpha = \epsilon_\alpha \Psi_\alpha \quad \text{or} \quad \{H_0 + V_{\text{ext}} + V_H\}|\alpha) = \epsilon_\alpha |\alpha)$$

and assume we know the solutions to

$$\{H_0 + V_{\text{ext}}\}\phi_\alpha = E_\alpha \phi_\alpha \quad \text{or} \quad \{H_0 + V_{\text{ext}}\}|\alpha\rangle = E_\alpha |\alpha\rangle$$

We know $\{\ |\alpha\rangle, E_\alpha\ \}$ and need to find $\{\ |\alpha), \epsilon_\alpha\ \}$

The eigenstates $\{\ |\alpha\rangle\ \}$ form a complete orthonormal basis

$$\sum_\alpha |\alpha\rangle\langle\alpha| = \mathbf{1} \quad \leftrightarrow \quad \sum_\alpha \phi^*_\alpha(\mathbf{r})\phi_\alpha(\mathbf{r}') = \delta(\mathbf{r}-\mathbf{r}')$$

So we can expand

$$|\alpha) = \sum_\beta |\beta\rangle\langle\beta|\alpha\rangle = \sum_\beta C_{\beta\alpha}|\beta\rangle \quad \leftrightarrow \quad \Psi_\alpha(\mathbf{r}) = \sum_\beta C_{\beta\alpha}\phi_\beta(\mathbf{r})$$

To find the coefficients $C_{\alpha\beta}$ we take the inner product of the equation of motion with $\langle\beta|$ and expand $|\alpha)$ as indicated above

The equation of motion transforms into

$$\langle\beta|\{H_0 + H_{\text{ext}} + V_H\}\sum_\gamma C_{\gamma\alpha}|\gamma\rangle = \epsilon_\alpha \sum_\gamma C_{\gamma\alpha}\langle\beta|\gamma\rangle$$

or

$$\sum_\gamma \{E_\gamma \delta_{\beta,\gamma} + \langle\beta|V_H|\gamma\rangle\} C_{\gamma\alpha} = \epsilon_\alpha C_{\beta\alpha}$$

Eigenvalue problem for a matrix (infinite dimensional),
no approximation, no differential equations,
compare to perturbation theory.

IF $\alpha = 1, 2$ then

$$\begin{pmatrix} E_1 + \langle 1|V_H|1\rangle & \langle 1|V_H|2\rangle \\ \langle 2|V_H|1\rangle & E_2 + \langle 2|V_H|2\rangle \end{pmatrix} \begin{pmatrix} C_{1\alpha} \\ C_{2\alpha} \end{pmatrix} = \epsilon_\alpha \begin{pmatrix} C_{1\alpha} \\ C_{2\alpha} \end{pmatrix}$$

To use this equation numerically we do an **approximation**:

Truncate the basis $\{ |\alpha\rangle \}$

Can be a very high order approximation,

multi parameter variational approach

Test the accuracy by varying the basis size

Evaluation of $\langle\alpha|V_H|\beta\rangle$

Often the most time consuming part (CPU or human)

If the electron density $n(\mathbf{r})$ is explicitly calculated then

$$\langle\alpha|V_H|\beta\rangle = -\frac{e^2}{\kappa}\int d\mathbf{r}' n(\mathbf{r}')\int d\mathbf{r}\frac{\phi^*_\alpha(\mathbf{r})\phi_\beta(\mathbf{r})}{|\mathbf{r}'-\mathbf{r}|} = \int d\mathbf{r}' n(\mathbf{r}') I(\mathbf{r},\mathbf{r}')$$

The density changes in each iteration (see later), but the kernel $I(\mathbf{r},\mathbf{r}')$ remains unchanged!

$I(\mathbf{r},\mathbf{r}')$ is often tricky and expensive to evaluate.

If $n(\mathbf{r})$ has a certain symmetry, translation or rotation invariance, then that part of the $\mathbf{r}'$ integration should be done analytically

Example: Infinite 2D strip of width L_y: Do the x-integration

$$\langle\alpha|V_H|\beta\rangle = -\frac{2e^2}{\kappa}\int dy' n(y') \int dy \phi^*_\alpha(y)\phi_\beta(y) \ln\left|\frac{y-y'}{L_y}\right|$$

Example: Circular symmetry 2D disk: Do the θ-integration

$$\langle\alpha|V_H|\beta\rangle = -\frac{4e^2}{\kappa}\int dr' n(r') \int_0^\infty \phi^*_\alpha(r)\phi_\beta(r) T(r,r')$$

with

$$T(r,r') = \left\{\Theta(r-r')\frac{r'}{r}K(\frac{r'}{r}) + \Theta(r'-r)K(\frac{r}{r'})\right\}$$

$K(x)$ is a complete elliptic integral (GR: 8.112)

Why are these expressions easier to use?

- Fewer dimensions to integrate over
- $K(x)$ can be expanded as a series of logarithms, logarithmic singularities are very easy to integrate analytically or numerically!

In systems without similar symmetries the integral of the $1/|\mathbf{r}-\mathbf{r}'|$ kernel is difficult and one should consider expansions as:

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = 4\pi \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \frac{1}{2l+1} \left(\frac{r_<^l}{r_>^{l+1}} \right) Y_{lm}^*(\theta', \phi') Y_{lm}(\theta, \phi)$$

for spherical coordinates (r, θ, ϕ)

and for cylindrical coordinates (ρ, ϕ, z)

$$\frac{1}{|\mathbf{r}-\mathbf{r}'|} = \sum_{m=-\infty}^{\infty} \int_0^{\infty} dk e^{im(\phi-\phi')} J_m(k\rho) J_m(k\rho') e^{-k(z_>-z_<)}$$

Here $x_<$ ($x_>$) is the smaller (larger) of x or x'

$1/|\mathbf{r}-\mathbf{r}'|$ is the Green function for the Poisson equation in an isotropic infinite space. Other expansions appropriate for different geometry and setups can be found by expanding the Green function in appropriate eigenfunctions, see Jackson CED chapter 3.12 in the 2nd ed.

Good numerical work includes a lot of analytical preparation!

Sometimes $n(\mathbf{r})$ is not of primary interest, f. ex. in HFA or exact numerical diagonalization, but the wave functions are:

$$\begin{aligned} n_s(\mathbf{r}) &= \sum_\alpha f(\varepsilon_\alpha)|\Psi_\alpha(\mathbf{r})|^2 \\ &= \sum_\alpha f(\varepsilon_\alpha) \sum_{p,q} C^*_{\alpha p} C_{\alpha q} \phi^*_p(\mathbf{r}) \phi_q(\mathbf{r}) \\ &= \sum_\alpha f(\varepsilon_\alpha) \sum_{p,q} C_{\alpha p} C_{\alpha q} \phi^*_p(\mathbf{r}) \phi_q(\mathbf{r}) \end{aligned}$$

An example is the matrix element for a 2D quantum dot in a magnetic field calculated by Ingibjörg Magnúsdóttir (http://www.raunvis.hi.is/reports/1999/RH-08-99.html)

$$\langle k|V_H|l\rangle = \frac{e^2}{4\pi\epsilon_r\epsilon_0}\gamma_k\gamma_l \sum_{\alpha} f_\alpha \sum_{p,q} C_{\alpha p}C_{\alpha q}\gamma_p\gamma_q \sum_{\kappa=0}^{k_r}\sum_{\lambda=0}^{l_r}\sum_{\nu=0}^{n_r}\sum_{\mu=0}^{m_r} \frac{(-1)^{\kappa+\lambda+\nu+\mu}}{\kappa!\lambda!\nu!\mu!}$$

$$\times \binom{k_r+|K|}{k_r-\kappa}\binom{l_r+|L|}{l_r-\lambda}\binom{n_r+|M|}{n_r-\nu}\binom{m_r+|N|}{m_r-\mu}$$

$$\times \frac{1}{2}\frac{\Gamma\left(\frac{L-K+|K|+|L|}{2}+\kappa+\lambda+1\right)}{\Gamma(L-K+1)}\frac{\Gamma\left(\frac{M-N+|M|+|N|}{2}+\nu+\mu+1\right)}{\Gamma(M-N+1)}$$

$$\times \int_0^\infty dk(ka)^{2(L-K)}$$

$$\times {}_1F_1\left(\frac{L-K+|K|+|L|}{2}+\kappa+\lambda+1; L-K+1; -\frac{k^2a^2}{2}\right)$$

$$\times {}_1F_1\left(\frac{M-N+|M|+|N|}{2}+\nu+\mu+1; M-N+1; -\frac{k^2a^2}{2}\right)$$

where $p=(M,n_r)$, $q=(N,m_r)$, $l=(L,l_r)$, and $k=(K,k_r)$,
$\gamma_k=\sqrt{k_r!/(|K|+k_r)!}$,
$L-K=M-N$, if $K>L$ and $N>M$ then $p\leftrightarrow q$

The last integral can be done analytically, but numerical integration is faster than the evaluation of the result.

We need to map a set of quantum numbers f. ex. (n, l, m, s) on a single index i, or more complex mapping in absorption calculations.

Iterations

$\langle\alpha|V_H|\beta\rangle$ depends on the solutions of $H|\alpha) = \epsilon_\alpha|\alpha)$, but is also needed there since $H = H_0 + V_{\text{ext}} + V_H$.

Exact solutions to the nonlinear problem are not known in most cases

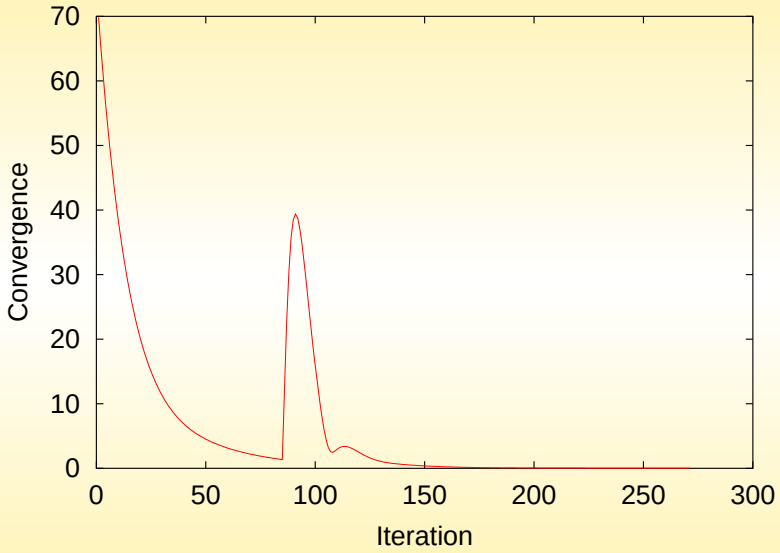
To use the linear algebra we use iterations:
Guess at $n(\mathbf{r})$, solve $H|\alpha) = \epsilon_\alpha|\alpha)$, use the solution to make new $\langle\alpha|V_H|\beta\rangle$, continue until $n^N(\mathbf{r}) \approx n^{N+1}(\mathbf{r})$

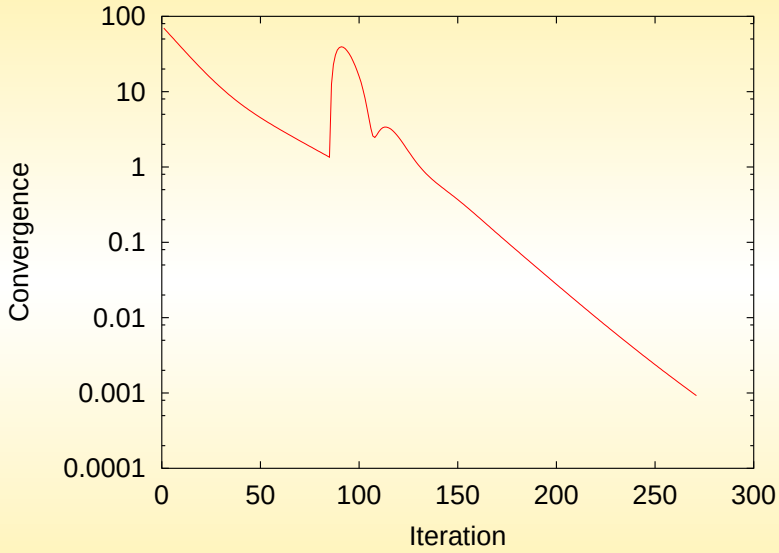
Hope the iteration gives the exact solution

- Most often these simple minded iterations are not convergent!
- Simple solution is often damping the change between iterations: $n(\mathbf{r}) = \varepsilon n^{\text{new}}(\mathbf{r}) + (1-\varepsilon) n^{\text{old}}(\mathbf{r})$.
- The system might get stuck in a state that is not the ground state, (HFA) $\rightarrow$ vary initial conditions.
- Instead of the primary quantity $n(\mathbf{r})$ one might use $V_H(\mathbf{r})$, or $\langle \alpha | V_H | \beta \rangle$.

Many sophisticated methods exist for each of these problems, see research literature.

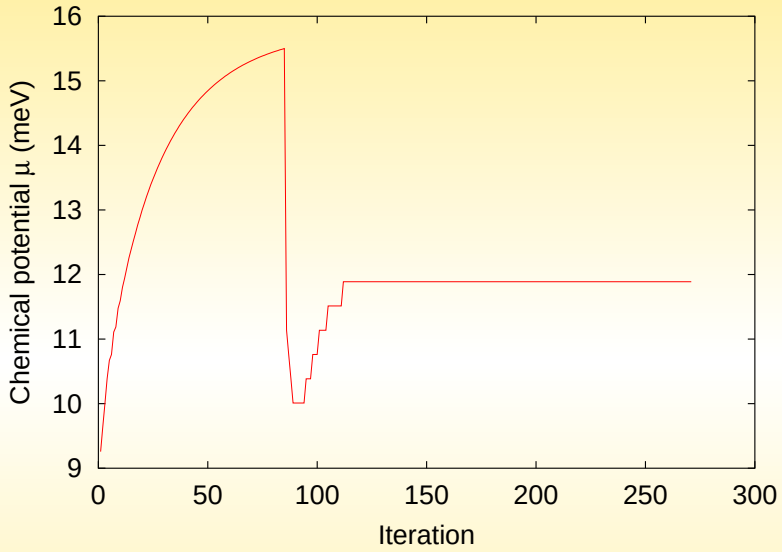
Example: 2 electrons in a quantum dot, **HFA**





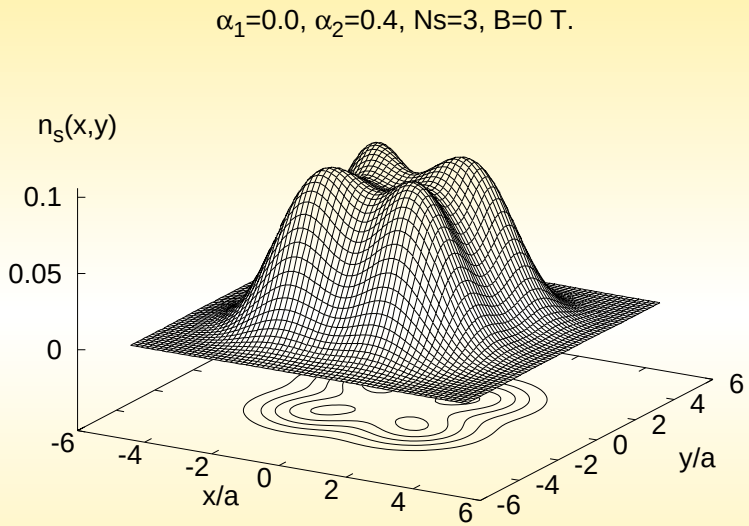
The exchange interaction starts at iteration 85

Behavior of the chemical potential μ.

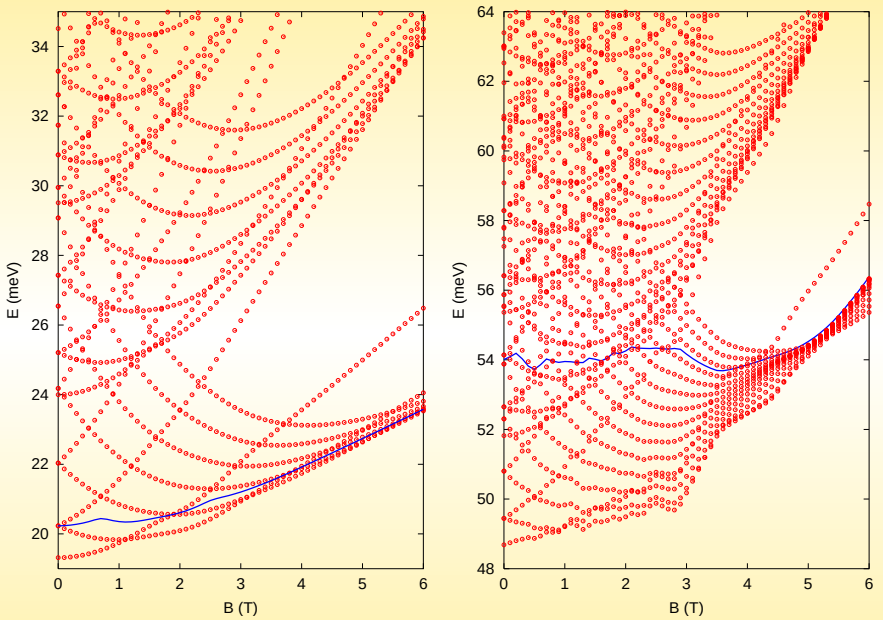


With the exchange interaction turned on, the system jumps between states.
In the HA the change is continuous

In systems with a neutralizing background, the HFA converges faster. in other systems the exchange can make the convergence more problematic.



Density of 3 electrons in
a dot with square symmetry



Energy spectra of a finite width
quantum ring with 2 or 12 electrons