Lesson 6 - Quantum Many-Body Systems
Unit 6.3 Hartree-Fock method for bosons and fermions

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Variational principle (I)

Theorem: For any normalized many-body state $|\Psi\rangle$, i.e. such that $\langle\Psi|\Psi\rangle = 1$, which belongs to the Hilbert space on which acts the Hamiltonian $\hat{H}$, one finds

$$\langle\Psi|\hat{H}|\Psi\rangle \geq E_{gs} \ , \tag{1}$$

where E_{gs} is the ground-state energy of the system and the equality holds only if $|\Psi\rangle = |\Psi_{gs}\rangle$ with $|\Psi_{gs}\rangle$ ground-state of the system, i.e. such that $\hat{H}|\Psi_{gs}\rangle = E_{gs}|\Psi_{gs}\rangle$.

Proof: The many-body Hamiltonian $\hat{H}$ satisfies the exact eigenvalue problem

$$\hat{H}|\Psi_\alpha\rangle = E_\alpha|\Psi_\alpha\rangle \ , \tag{2}$$

where E_α are the ordered eigenvalues, i.e. such that $E_0 < E_1 < E_2 < ...$ with $E_0 = E_{gs}$, and $|\Psi_\alpha\rangle$ the corresponding orthonormalized eigenstates, i.e. such that $\langle\Psi_\alpha|\Psi_\beta\rangle = \delta_{\alpha,\beta}$ with $|\Psi_0\rangle = |\Psi_{gs}\rangle$.

Variational principle (II)

The generic many-body state $|\Psi\rangle$ can be written as

$$|\Psi\rangle = \sum_{\alpha} c_{\alpha} |\Psi_{\alpha}\rangle \ , \tag{3}$$

where c_{α} are the complex coefficients of the expansion such that

$$\sum_{\alpha} |c_{\alpha}|^2 = 1 \ . \tag{4}$$

Then one finds

$$\begin{aligned} \langle \Psi | \hat{H} | \Psi \rangle &= \sum_{\alpha,\beta} c_{\alpha}^{*} \ c_{\beta} \ \langle \Psi_{\alpha} | \hat{H} | \Psi_{\beta} \rangle = \sum_{\alpha,\beta} c_{\alpha}^{*} \ c_{\beta} \ E_{\beta} \ \langle \Psi_{\alpha} | \Psi_{\beta} \rangle \\ &= \sum_{\alpha,\beta} c_{\alpha}^{*} \ c_{\beta} \ E_{\beta} \ \delta_{\alpha,\beta} = \sum_{\alpha} |c_{\alpha}|^2 \ E_{\alpha} \\ &\geq \sum_{\alpha} |c_{\alpha}|^2 \ E_0 = E_{gs} \ , \end{aligned} \tag{5}$$

with $E_0 = E_{gs}$. Obviously, the equality holds only if $c_0 = 1$ and, consequently, all the other coefficients are zero.

Hartree for bosons (I)

In 1927 by Douglas Hartree and Vladimir Fock used the variational principle to develop a powerful method for the study of interacting identical particles.
In the case of N identical interacting bosons the Hartree approximation is simply given by

$$\Psi(x_1, x_2, ..., x_N) = \phi(x_1)\ \phi(x_2)\ ...\ \phi(x_N)\ , \tag{6}$$

where the single-particle wavefunction $\phi(x)$ must be determined in a self-consistent way. This factorization implies that all particles belong to the same single-particle state, i.e. the interacting system is a pure Bose-Einstein condensate.
The unknown wavefunction $\phi(x)$ is determined by minimizing the expectation value of the total Hamiltonian, given by

$$\langle\Psi|\hat{H}|\Psi\rangle = \int dx_1 dx_2 ... dx_N \Psi^*(x_1, x_2, ..., x_N)\hat{H}\Psi(x_1, x_2, ..., x_N)\ , \tag{7}$$

with respect to $\phi(x)$.

Hartree for bosons (II)

The quantum Hamiltonian of N identical interacting particles is given by

$$\hat{H} = \sum_{i=1}^{N} \hat{h}(x_i) + \frac{1}{2} \sum_{\substack{i,j=1 \\ i \neq j}}^{N} V(x_i, x_j) = \hat{H}_0 + \hat{H}_I \ , \tag{8}$$

where $\hat{h}$ is the single-particle Hamiltonian and $V(x_i, x_j)$ is the inter-particle potential of the mutual interaction. From the Hartree ansatz one finds immediately

$$\begin{aligned} \langle \Psi | \hat{H} | \Psi \rangle &= N \int dx \ \phi^*(x) \hat{h}(x) \phi(x) \\ &+ \frac{1}{2} N(N-1) \int dx \ dx' \ |\phi(x)|^2 V(x, x') |\phi(x')|^2 \ , \end{aligned} \tag{9}$$

which is a nonlinear energy functional of the single-particle wavefunction $\phi(x)$. It is called single-orbital Hartree functional for bosons.

Hartree for bosons (III)

We minimize the Hartree functional of bosons with the following constraint due to the normalization

$$\int dx \; |\phi(x)|^2 = 1 \; . \tag{10}$$

We get immediately the so-called Hartree equation for bosons

$$\left[\hat{h}(x) + (N-1) \int dx' \; V(x,x') \; |\phi(x')|^2 \right] \phi(x) = \epsilon \; \phi(x) \; , \tag{11}$$

where ϵ is the Lagrange multiplier fixed by the normalization.
In the case of spinless bosons, where $|x\rangle = |\mathbf{r}\rangle$, given the local bosonic density

$$\rho(\mathbf{r}) = N|\phi(\mathbf{r})|^2 \; , \tag{12}$$

under the assumption $N \gg 1$ the Hartree equation becomes

$$\left[-\frac{\hbar^2}{2m}\nabla^2 + U(\mathbf{r}) + \int d^3\mathbf{r}' \; V(\mathbf{r}-\mathbf{r}') \; \rho(\mathbf{r}') \right] \phi(\mathbf{r}) = \epsilon \; \phi(\mathbf{r}) \; . \tag{13}$$

Hartree-Fock for fermions (I)

In the case of N identical interacting fermions, the approximation developed by Hartree and Fock is based on the Slater determinant we have seen previously, namely

$$\Psi(x_1, x_2, ..., x_N) = \frac{1}{\sqrt{N!}} \begin{pmatrix} \phi_1(x_1) & \phi_1(x_2) & ... & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & ... & \phi_2(x_N) \\ ... & ... & ... & ... \\ \phi_N(x_1) & \phi_N(x_2) & ... & \phi_N(x_N) \end{pmatrix} , \quad (14)$$

where now the single-particle wavefunctions $\phi_n(x)$ are unknown and they are determined with a variational procedure.
In particular, the wavefunctions $\phi_n(x)$ are obtained by minimizing the expectation value of the total Hamiltonian, given by

$$\langle \Psi | \hat{H} | \Psi \rangle = \int dx_1 \; dx_2 \; ... \; dx_N \; \Psi^*(x_1, x_2, ..., x_N) \hat{H} \Psi(x_1, x_2, ..., x_N) \; , \quad (15)$$

with respect to the N single-particle wavefunctions $\phi_n(x)$.

Hartree-Fock for fermions (II)

After some tedious calculations one finds

$$\begin{aligned}\langle\Psi|\hat{H}|\Psi\rangle &= \sum_{i=1}^{N}\int dx\ \phi_i^*(x)\hat{h}(x)\phi_i(x) \\ &+ \frac{1}{2}\sum_{\substack{i,j=1\\ i\neq j}}^{N}\Big[\int dx\ dx'\ |\phi_i(x)|^2 V(x,x')|\phi_j(x')|^2 \\ &- \int dx\ dx'\ \phi_i^*(x)\phi_j(x)V(x,x')\phi_j^*(x')\phi_i(x')\Big]\,, \qquad (16)\end{aligned}$$

which is a nonlinear energy functional of the N single-particle wavefunctions $\phi_i(x)$. The first term is related to the single-particle Hamiltonian $\hat{h}(x)$. The second term is called direct term of interaction and the third term is called exchange term of interaction.
We minimize this functional with the following constraints due to the normalization

$$\int dx\ |\phi_i(x)|^2 = 1\,, \qquad i = 1, 2, ..., N\,. \qquad (17)$$

Hartree-Fock for fermions (III)

After minimization of the energy functional we get the so-called Hartree-Fock equations

$$\hat{h}(x)\phi_i(x) + U_d(x)\ \phi_i(x) - \sum_{j=1}^{N} U_x^{ji}(x)\phi_j(x) = \epsilon_i\ \phi_i(x) \tag{18}$$

where ϵ_i are the Lagrange multipliers fixed by the normalization and $\hat{U}_{mf}$ is a nonlocal mean-field operator. The direct mean-field potential $U_d(x)$ reads

$$U_d(x) = \sum_{\substack{j=1 \\ j\neq i}}^{N} \int dx'\ V(x,x')\ |\phi_j(x')|^2\ , \tag{19}$$

while the exchange mean-field potential $U_x^{ji}(x)$ is instead

$$U_x^{ji}(x) = \int dx'\ \phi_j^*(x')\ V(x,x')\ \phi_i(x')\ . \tag{20}$$