Quantum Mechanics in a nutshell and Hartree-Fock

Electrostatics

the Yambo team
Quantum Mechanics made short

The Many-Body Problem

Hartree-Fock
The Many-Body Problem: a micro-macro connection

\[ H = \sum_i h(x_i, p_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|} \]
A (very) hard job!

\[ \langle N | = (| N \rangle) \]

\[ A = \langle N | \hat{A} | N \rangle \]

\[ | N(t) \rangle = U(t, t_0) | N(t_0) \rangle \]

Diagrams
Why so many bodies?

\[ H = \sum_i h(x_i, p_i) + \frac{1}{2} \sum_{i \neq j} \left| x_i - x_j \right|^{-1} \]
Bra's, ket's and operators
Bra, Ket and operators

A ket represents a physical state (atomic configuration, Bloch level, ...) and it contains ALL we need to know about the state

\[
H = \sum_i h(x_i, p_i) + \frac{1}{2} \sum_{i \neq j} \frac{1}{|x_i - x_j|^{-1}} 
\]

\[
\hat{h} |n\rangle = \epsilon_n |n\rangle \\
\hat{H} |N\rangle = E_N |N\rangle
\]
Any observable is represented by an operator acting in the space of kets

\[ \hat{A} |N\rangle = |N'\rangle \]
Observables and eigenstates

\[ A = \langle N | \hat{A} | N \rangle \]

- Position
- Speed
- Energy
- Current
- Polarization

\[ \hat{A} | N \rangle = A_N | N \rangle \]

- Molecular Orbital
- Gas of electrons
- Electronic band

- "Expectation value"
- "Eigenstate"

\[ A = A_N \]
The Many-Body Problem: a micro-macro connection

\[ A = \langle N | \hat{A} | N \rangle \]
Independent Particle Approximation

\[ H = \sum_i h(x_i) + \frac{1}{2} \sum_{i \neq j} |x_i - x_j|^{-1} \]

\[ \hat{h}|n\rangle = \epsilon_n |n\rangle \]

\[ |N\rangle \approx D_N[|n\rangle] \]

\[ |N=0\rangle \approx \prod_n^{\text{filled}} |n\rangle \]

\[ \langle N \| \hat{A} \| N \rangle \approx F_N[\{A_n\}] \]

\[ \langle N=0 \| \hat{H} \| N=0 \rangle \approx \sum_n \epsilon_n \]
Many Bodies and Many environments

Full Hamiltonian

Zero Temperature

Static Hamiltonian

Ground State

\[ |\Phi\rangle = |N=0\rangle \]
Many-Body Methods

\[ H = \sum_i h(x_i) + \frac{1}{2} \sum_{i \neq j} |x_i - x_j|^{-1} = h + H' \]

The objective of most of the Many Body methods is to rewrite the fully interacting problem as an as much independent as possible counter-part.
Many-Body Methods

\[ H = \sum_i h(x_i) + \frac{1}{2} \sum_{i \neq j} |x_i - x_j|^{-1} \]

\[ H \approx \sum_i h(x_i) \]

\[ H \approx \sum_i \left( h(x_i) + V_{MB}[\{x_j\}] \right) \]

The objective of the Many Body methods is to define (if it exists) \( V_{MB} \).
"Time" evolution operator
Schrödinger and Heisenberg representations

\[ |\Phi(t_0)\rangle \quad \text{Time Evolution} \quad |\Phi(t)\rangle = U(t, t_0) |\Phi(t_0)\rangle \]

\[ i \partial_t |\Phi(t)\rangle = \hat{H}(t) |\Phi(t)\rangle \quad \text{Schrödinger equation} \]

\[ |\Phi_s(t)\rangle = e^{-i\hat{H}(t-t_0)} |\Phi(t_0)\rangle \quad U(t, t_0) = e^{-i\hat{H}(t-t_0)} \quad \text{States (Schrödinger)} \]

\[ |\Phi(t)\rangle = e^{i\hat{H}t} |\Phi_s(t)\rangle \quad \hat{O}_H(t) = e^{i\hat{H}t} \hat{O} e^{-i\hat{H}t} \quad \text{Operators (Heisenberg)} \]
Independent Particle Approximation

\[ H = \sum_i h(x_i) + \frac{1}{2} \sum_{i \neq j} |x_i - x_j|^{-1} \]

\[ |\Phi(t)\rangle = e^{i \sum_n \epsilon_n (t - t_0)} |N(t_0)\rangle \]
The limiting case of one-particle potentials

\[ H = \sum_i h(x_i) + \frac{\lambda}{2} \sum_{i \neq j} |x_i - x_j|^{-1} \]

\[ |N\rangle \approx \sum_{n,m}^{\infty} C_{Nn}^m \lambda^m |n_m\rangle \]

Introduction to Perturbation Methods:
The limiting case of one-particle potentials

\[ H \approx \sum_i (h(x_i) + \delta h(x_i)) \]
The two-level problem

\[ h + H' = E_1^{(0)} |1(0)\rangle \langle 1(0)| + E_2^{(0)} |2(0)\rangle \langle 2(0)| + V (|1(0)\rangle \langle 2(0)| + |2(0)\rangle \langle 1(0)|) \]

We want to find the states \( |n\rangle \) such that:

\[ h + H' = E_1 |1\rangle \langle 1| + E_2 |2\rangle \langle 2| \]

The problem can be solved by direct diagonalization of the matrix

\[
\begin{pmatrix}
E_1^{(0)} & V \\
V & E_2^{(0)}
\end{pmatrix}
\]

\[ E_{1/2} = \frac{E_1^{(0)} + E_2^{(0)}}{2} \pm \sqrt{\frac{E_1^{(0)} - E_2^{(0)}}{4} + V^2} \]
The two-level problem

\[ H(\lambda) = h + \lambda H' \]

\[ E_{1/2}(\lambda) = \frac{E_1^{(0)} + E_2^{(0)}}{2} \pm \sqrt{\frac{E_1^{(0)} - E_2^{(0)}}{4} + V(\lambda)^2} \]

\[ \lambda V^2 \ll |E_1^{(0)} - E_2^{(0)}| \]

\[ E_{1/2}(\lambda) = E_{1/2}^{(0)} \pm \frac{(V \lambda)^2}{E_1^{(0)} - E_2^{(0)}} + O(\lambda^4) \]

The question is: is it possible to obtain this power expansion without solving the full problem?
Static Perturbation Theory

\[ h + \lambda H' = \sum_n E_n^{(0)} |n^{(0)}\rangle \langle n^{(0)}| + \sum_{n,m} \lambda H'_{n,m} |n^{(0)}\rangle \langle m^{(0)}| \]

Now the PT is easily introduced by the following set of definitions

\[ |n\rangle_\lambda = \sum_{m=0}^\infty \lambda^m |n^{(m)}\rangle \]

\[ (h + \lambda H') |n(\lambda)\rangle \langle n(\lambda)| = E_n(\lambda) |n(\lambda)\rangle \langle n(\lambda)| \]

\[ E_n(\lambda) - E^{(0)} = \sum_{m=0}^\infty \lambda^m \Delta E_n^{(m)} \]

\[ |n(\lambda)\rangle \approx |n^{(0)}\rangle + \sum_{k \neq n} \frac{H'_{kn}}{E_n^{(0)} - E_k^{(0)}} + \ldots \]

\[ E_n(\lambda) \approx E_n^{(0)} + \lambda H'_{nn} + \sum_{k \neq m} \lambda^2 \frac{|H'_{nk}|^2}{E_n^{(0)} - E_k^{(0)}} + \ldots \]
Static Perturbation Theory

\[ h + H' = E_1^{(0)} |1^{(0)}\rangle \langle 1^{(0)}| + E_2^{(0)} |2^{(0)}\rangle \langle 2^{(0)}| + V (|1^{(0)}\rangle \langle 2^{(0)}| + |2^{(0)}\rangle \langle 1^{(0)}|) \]

\[ E_n(\lambda) \approx E_n^{(0)} + \lambda H'_m + \sum_{k \neq m} \lambda^2 \frac{|H'_{nk}|^2}{E_n^{(0)} - E_k^{(0)}} + \ldots \]

\[ E_{1/2}(\lambda) = E_{1/2}^{(0)} \pm \frac{(V \lambda)^2}{E_1^{(0)} - E_2^{(0)}} + O(\lambda^4) \]

By using PT I can find again the first order in the perturbative expansion of the exact solution.
Static Perturbation Theory: The Zeeman Effect

\[ H' = -\vec{\mu} \cdot \vec{B} \]
\[ \vec{\mu} = -\mu_B g \vec{J} \]

\[ E_n(\lambda) \approx E_n^{(0)} + \lambda H'_m \]
REAL many body interactions and FICTITIOUS quasi-particles
Perturbation Theory for Many-Body Systems

\[ H = \sum_i h(x_i) + \frac{1}{2} \sum_{i \neq j} |x_i - x_j|^{-1} \]

\[ H = \sum_i h(x_i) \]

\[ \left| \Phi \right| \approx \prod_n \left| n \right> \]

\[ H = \sum_i (h(x_i) + \delta h(x_i)) \]

\[ \left| \Phi \right| \approx \prod_n \left| n_{qp} \right> \]
Hartree-Fock
Hartree-Fock

\[ H = \sum_i h(x_i) + \frac{1}{2} \sum_{i \neq j} |x_i - x_j|^{-1} \]

\[ |\Phi\rangle \approx \prod_n |n\rangle = |\Phi_0\rangle \]

\[ \langle x_1 ... x_N | \Phi_0 \rangle \approx \sum_{\text{Permutations}} (-1)^p \prod_n \langle x_i | n \rangle \]

\[ E_n(\lambda) \approx E_n^{(0)} + \lambda H'_{nn} + \sum_{k \neq m} \lambda^2 \frac{|H'_{nk}|^2}{E_n^{(0)} - E_k^{(0)}} + ... \]

\[ E_\Phi = \langle \Phi | H | \Phi \rangle \approx E_{\Phi_0} + \langle \Phi_0 | H' | \Phi_0 \rangle \]
\[ E_\Phi = \langle \Phi | H | \Phi \rangle \approx E_{\Phi_0} + \langle \Phi | H' | \Phi \rangle \]

\[ E_\Phi \approx \sum_n \left( \epsilon_n^0 + \delta \epsilon_n^{HF} \right) \]

\[ \delta \epsilon_n^{HF} \equiv \langle n^0 | V_H(x) | n^0 \rangle - \langle n^0 | V_F(x, x') | n^0 \rangle \]

\[ V_H(x) = \sum_m \int dx' \frac{1}{|x-x'|} |x'| |m^0|^2 \]

\[ V_F(x, x') = \sum_m \frac{\langle x | m^0 \rangle \langle m^0 | x' \rangle}{|x-x'|} \]
Hartree–Fock via Variational Methods

If we concentrate on the fully interacting ground-state an approach alternative to perturbation theory is via variational minimization of the total Energy

\[ H = \sum_i h(x_i) + \frac{1}{2} \sum_{i \neq j} |x_i - x_j|^{-1} \]

The idea is to define a set of single-particle states such that the expectation value of \( H \) is minimal

\[ \langle x_1...x_N | \Phi_0 \rangle \approx \sum_{\text{Permutations}} (-1)^p \langle x_i | n \rangle \]

\[ L[\{\chi_n\}] \equiv \langle \Phi_0 | H | \Phi_0 \rangle - \sum_{nm} \lambda_{nm} \left( \langle n | m \rangle - \delta_{nm} \right) \]
Hartree–Fock via Variational Methods

\[ L[|\chi_n]\rangle \equiv \langle \Phi_0 | H | \Phi_0 \rangle - \sum_{nm} \lambda_{nm} (\langle n | m \rangle - \delta_{nm}) \]

\[ \delta L[|\chi_n]\rangle = 0 \quad \chi_n(x) \equiv \langle x | n \rangle \]

\[ h(x) \chi_n(x) + V_H(x) \chi_n(x) - \sum_m \int dx' V_F(x, x') \chi_m(x') = \epsilon_n^{HF} \chi_n(x) \]

\[ V_H(x) = \sum_m \int dx' \frac{1}{|x-x'|} |\langle x' | m \rangle|^2 \]

\[ V_F(x, x') = \sum_m \frac{\langle x | m \rangle \langle m | x' \rangle}{|x-x'|} \]
Hartree–Fock: take home messages

In the Perturbative approach
wavefunction do not change.
Only energies change.

HF is just the sum of
electrostatic and
exclusion principle

In the fully variational
approach energies and
wavefunctions are found
self–consistently

The “HF” potential is defined as the effective
potential which provides the first order
energies (PT approach) or which minimize the
total energy (variational approach)
Hartree-Fock: take home message

Molecules

Hartree Fock lacks of CORRELATION

= Electrostatics + +
1. Many-body perturbation theory calculations using the yambo code
2. Yambo: an ab initio tool for excited state calculations