Quantum Mechanics in a nutshell and Hartree-Fock

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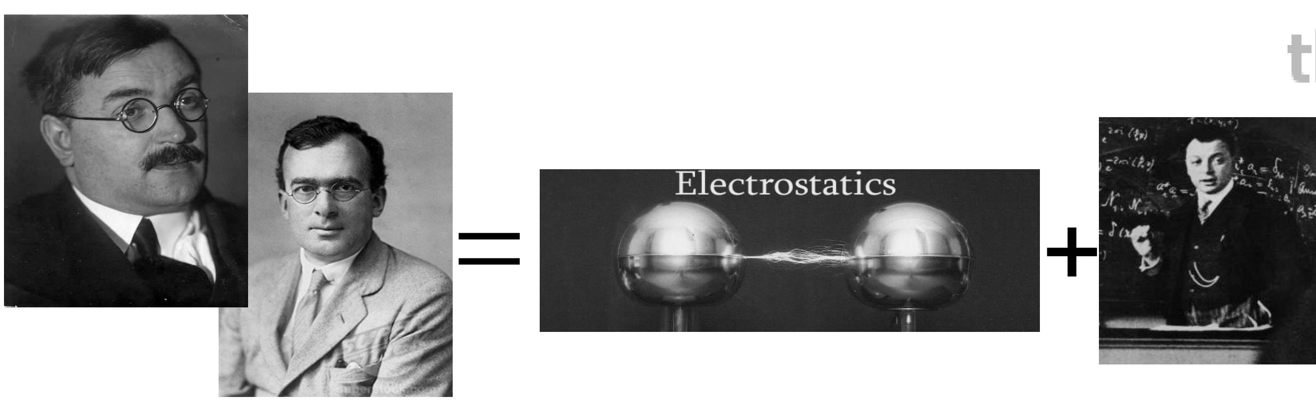
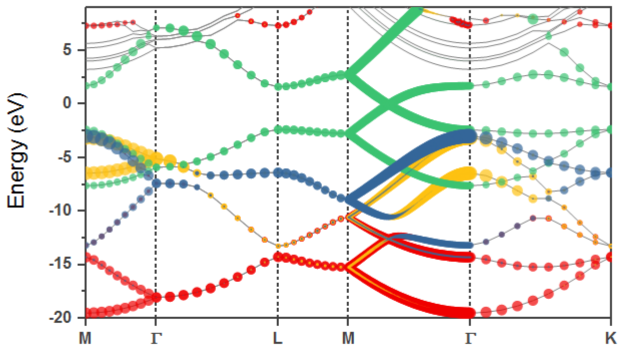


Quantum Mechanics made short

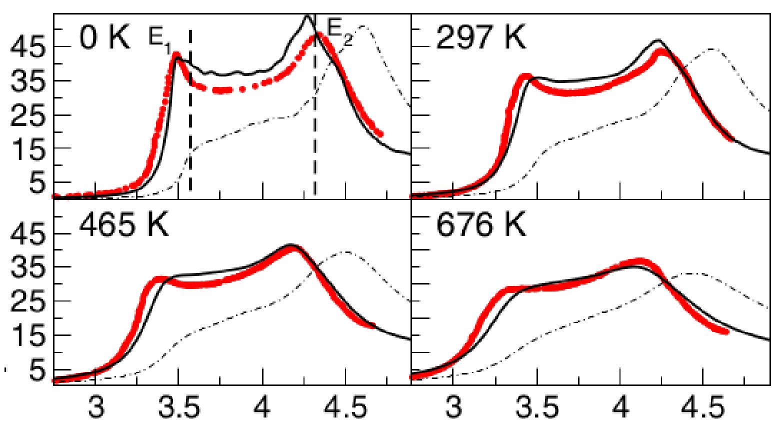
The Many-Body Problem

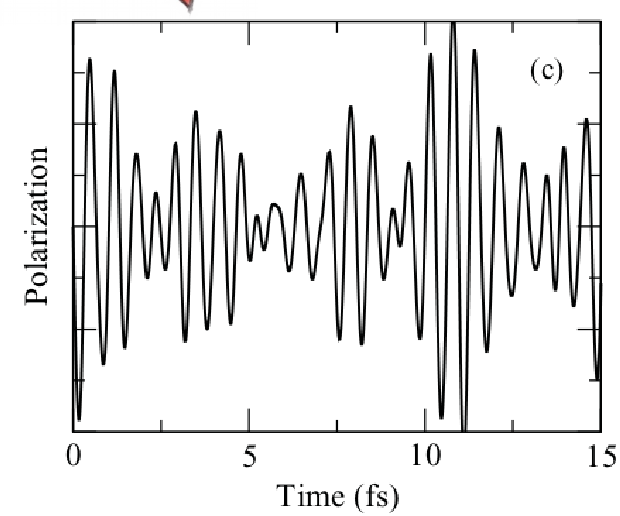
Hartree-Fock

The Many-Body Problem: a micro-macro connection



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





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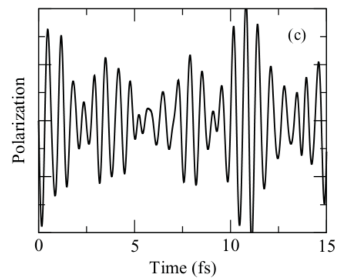
A (very) hard job!

$$\langle N| = \overline{(|N\rangle)}$$

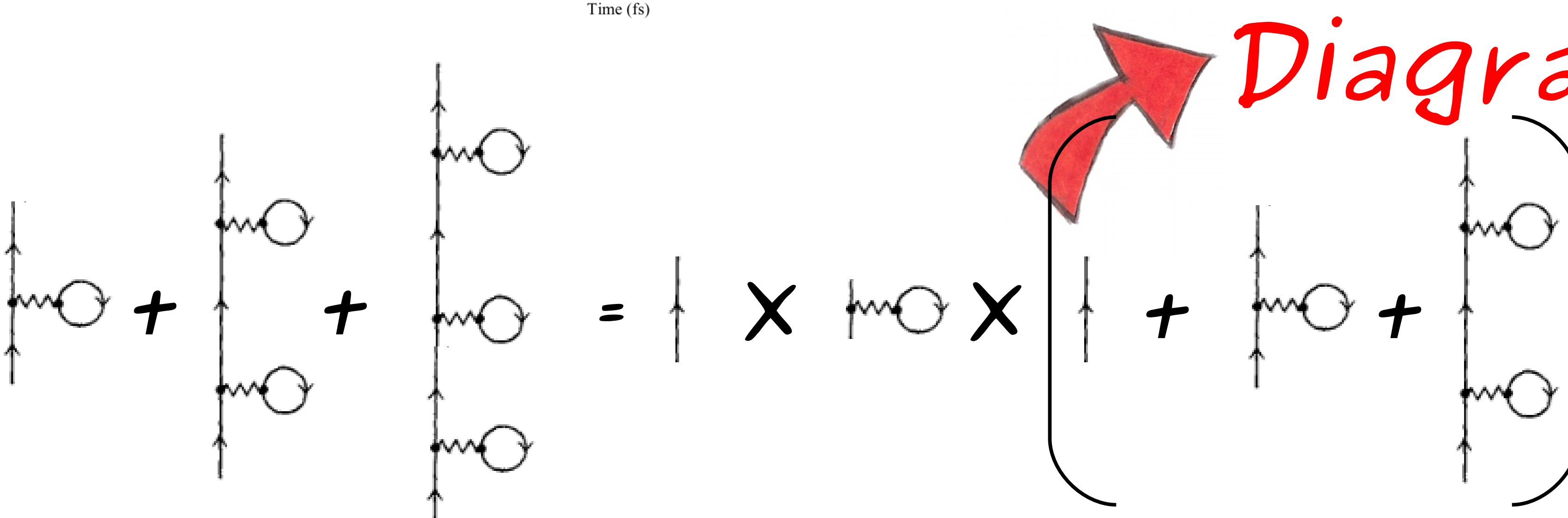
QM

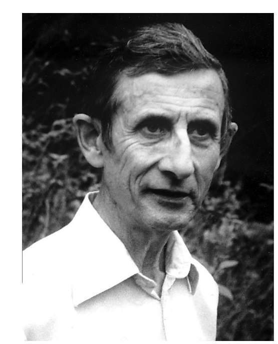
$$A = \langle N|\hat{A}|N\rangle$$



$$|N(t)\rangle = U(t,t_0)|N(t_0)\rangle$$

Diagrams





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Why so many bodies ?

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

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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

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

$$\hat{h}|n\rangle=\epsilon_n|n\rangle$$

$$\hat{H}|N\rangle=E_N|N\rangle$$

Bra, Ket and operators

"Ket" $\rightarrow$ $|N\rangle$

"Bra" $\rightarrow$ $\langle N| = \overline{(|N\rangle)}$

$\langle N|M\rangle$

$\langle N|N\rangle = |N|$

$\sum_N |N\rangle\langle N| = 1$

$\vdots$

Any observable is represented by an operator acting in the space of kets

$$\hat{A}|N\rangle = |N'\rangle$$

Observables and eigenstates

Position
Speed
Energy
Current
Polarization

$$A = \langle N | \hat{A} | N \rangle$$

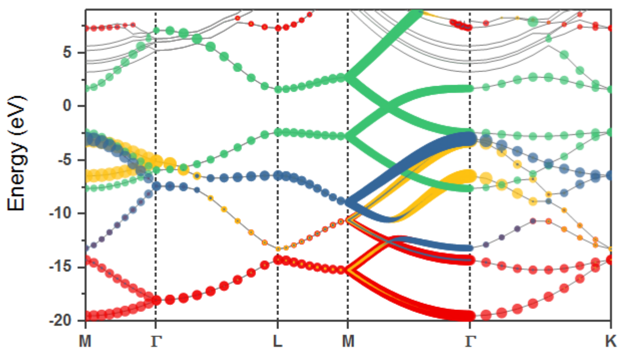
Molecular Orbital
Gas of electrons
Electronic band

"Expectation value"

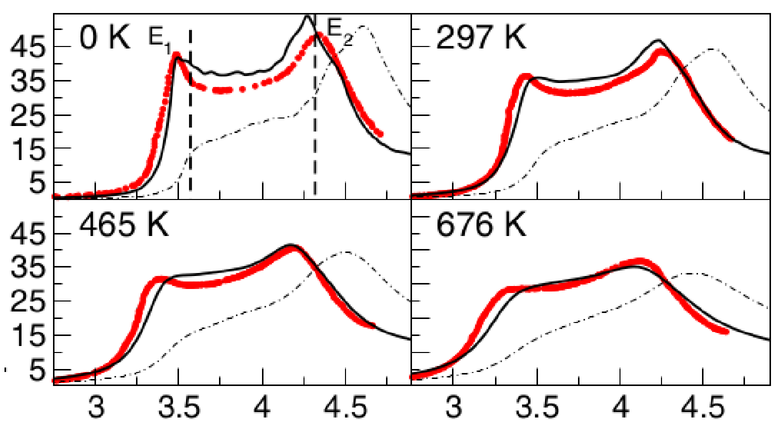
$$\hat{A} | N \rangle = A_N | N \rangle \longrightarrow A = A_N$$

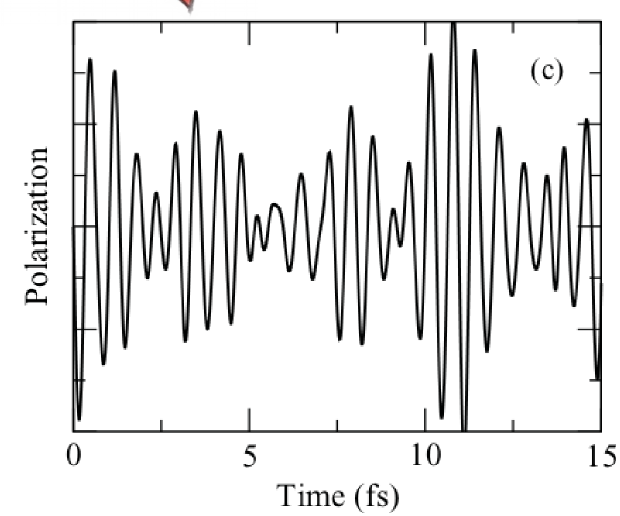
"Eigenstate"

The Many-Body Problem: a micro-macro connection



$$A = \langle N | \hat{A} | N \rangle$$





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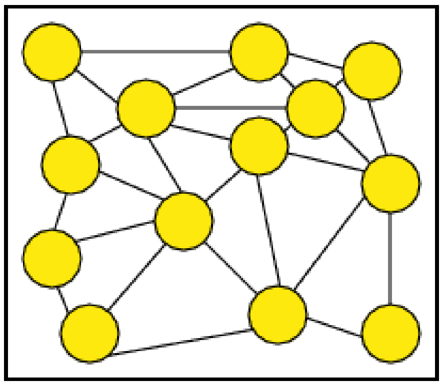
Independent Particle Approximation

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

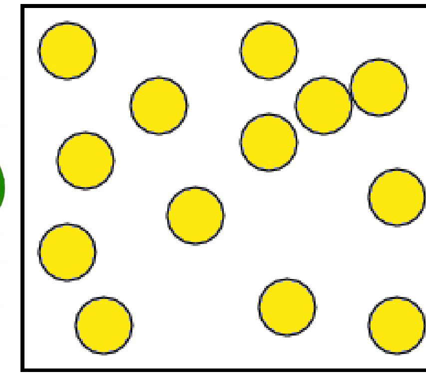
$$H=\sum_i h(x_i)$$



$$\hat{h}|n\rangle=\epsilon_n|n\rangle$$

$$|N\rangle\approx D_N\left[\left\{|n\rangle\right\}\right]$$

$$|N=0\rangle\approx\prod_n^{(filled)}|n\rangle$$



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

$$\langle N=0|\hat{H}|N=0\rangle\approx\sum_n\epsilon_n$$

Many Bodies and Many environments

Full Hamiltonian

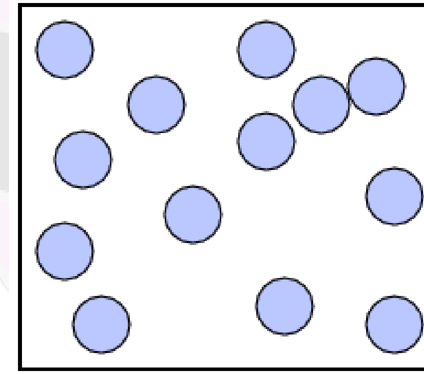
Zero Temperature

Static Hamiltonian

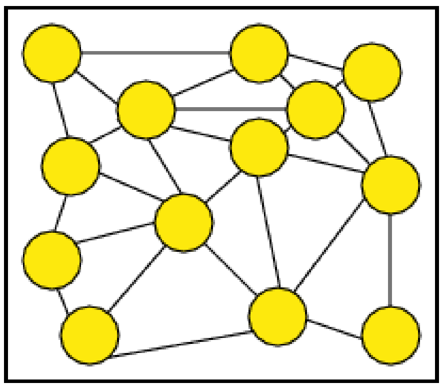
Ground State

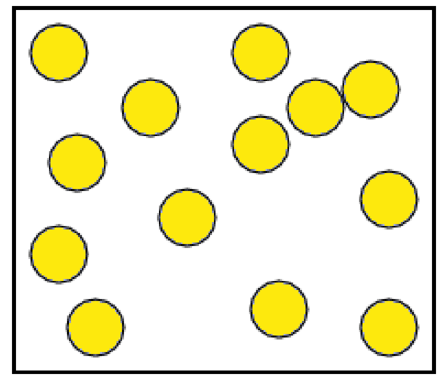
$$|\Phi\rangle = |N=0\rangle$$

Many-Body Methods



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





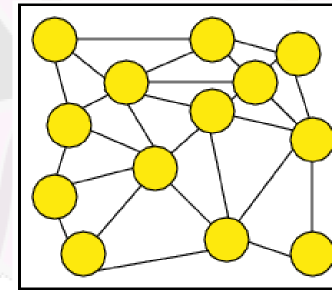
The objective of most of the Many Body methods is to rewrite the fully interacting problem as an as much independent as possible counter-part

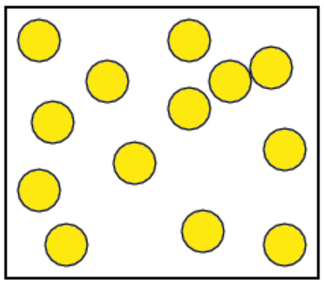
Bare particle

???

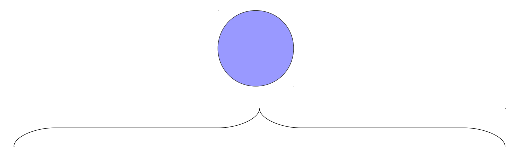
Many-Body Methods

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

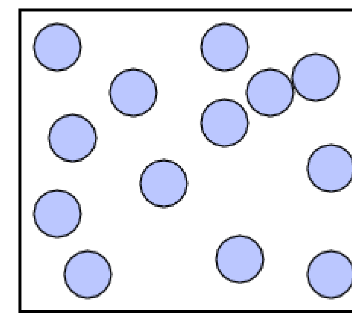




$$H \approx \sum_i h(x_i)$$



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



The objective of the Many Body methods is to define (if it exists) V_{MB}

"Time" evolution operator

Schördinger and Heisenberg representations

$|\Phi(t_0)\rangle$ → Time Evolution → $|\Phi(t)\rangle = U(t,t_0)|\Phi(t_0)\rangle$

$$i\partial_t|\Phi(t)\rangle = \hat{H}(t)|\Phi(t)\rangle$$

Schördinger equation

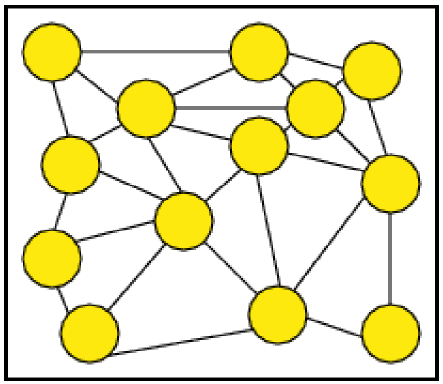
Time–Independent H

$\lvert\Phi_s(t)\rangle = \mathrm{e}^{-i\hat{H}(t-t_0)}\lvert\Phi(t_0)\rangle$	$U(t,t_0) = e^{-iH(t-t_0)}$	States (Schördinger)
$\lvert\Phi(t)\rangle = \mathrm{e}^{i\hat{H}t}\lvert\Phi_s(t)\rangle$	$\hat{O}_H(t) = \mathrm{e}^{i\hat{H}t}\hat{O}\,\mathrm{e}^{-i\hat{H}t}$	Operators (Heisenberg)

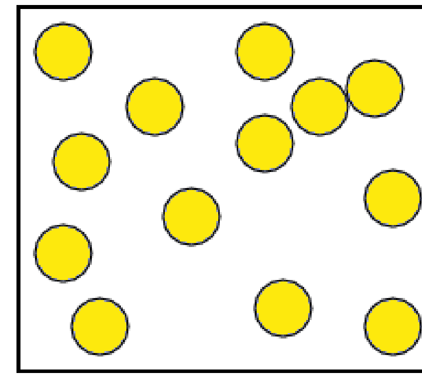
Independent Particle Approximation

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

$$H=\sum_i h(x_i)$$



$$|\Phi\rangle\approx\prod_n |n\rangle$$



$$\hat{h}|n\rangle=\epsilon_n|n\rangle$$

$$|n(t)\rangle=e^{i\epsilon_n(t-t_0)}|n(t_0)\rangle$$

$$|\Phi(t)\rangle=e^{i\left(\sum_n\epsilon_n\right)(t-t_0)}|N(t_0)\rangle$$

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

$$\left|N\right\rangle \approx \sum_{n,m}^{\infty} C_{Nn}^{m}\lambda^{m}\left|n_m\right\rangle$$

Introduction to Perurbation Methods:

The limiting case of one-particle potentials

$$H\approx\sum_i\left(h(x_i)+\delta h(x_i)\right)$$

The two-level problem

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

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

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

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

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

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

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

Static Perturbation Theory

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

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

0 (H'_{nn})

V^2 ($|H'_{nk}|^2$)

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

By using PT I can find again the first order in the perturbative expansion of the exact solution

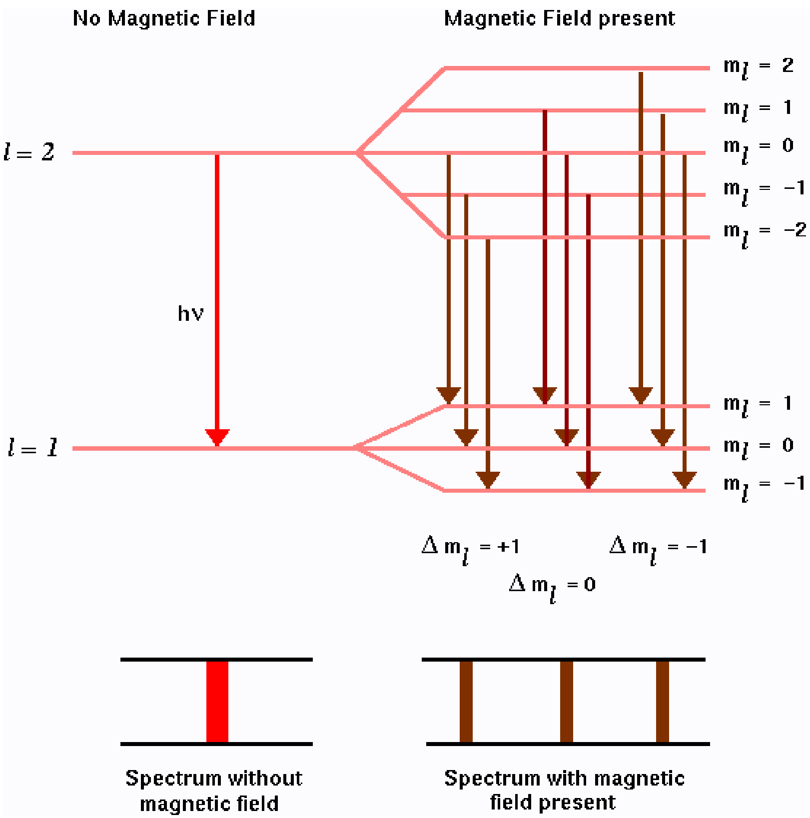
Static Perturbation Theory: The Zeeman Effect

H'
- Static Electric Field
- Static Magnetic Field
- Stress
- ...

$$H' = -\vec{\mu} \cdot \vec{B}$$

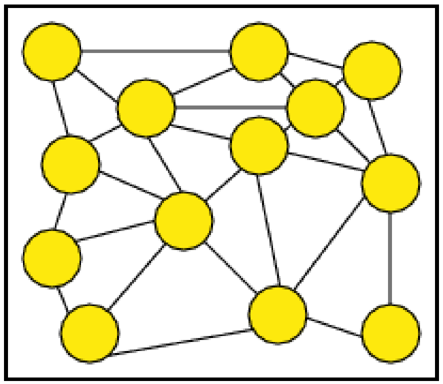
$$\vec{\mu} = -\mu_B g \vec{J}$$

$$E_n(\lambda) \approx E_n^{(0)} + \lambda H'_{nn}$$



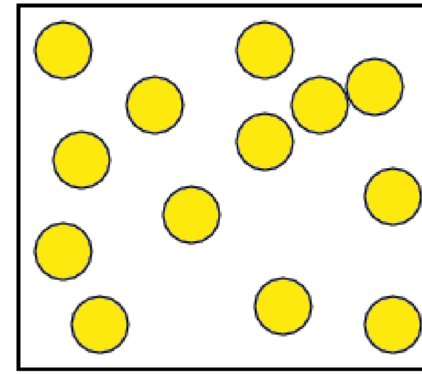
Perturbation Theory for Many-Body Systems

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

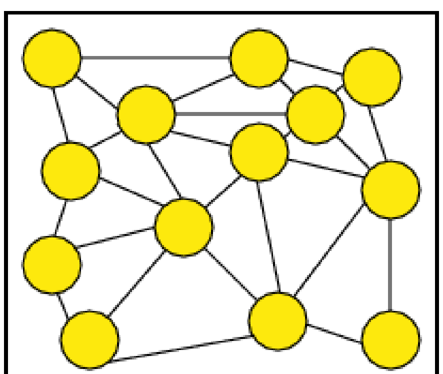


$$|\Phi\rangle\approx\prod_n|n\rangle$$

$$H=\sum_i h(x_i)$$

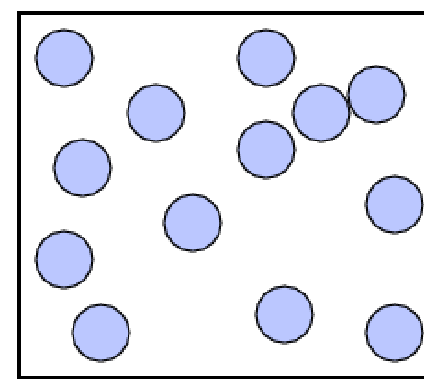


$$H=\sum_i h(x_i)+\frac{1}{2}\sum_{i\neq j}|x_i-x_j|^{-1}$$



$$|\Phi\rangle\approx\prod_n|n_{qp}\rangle$$

$$H=\sum_i\left(h(x_i)+\delta h(x_i)\right)$$



Hartree-Fock

Hartree-Fock

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

H'

$$|\Phi\rangle\approx\prod_n|n\rangle=|\Phi_0\rangle$$

$$\langle x_1\ldots x_N|\Phi_0\rangle\approx\sum_{Permutations}(-1)^P\prod_n\langle x_i|n\rangle$$

$\chi_n(x_i)$

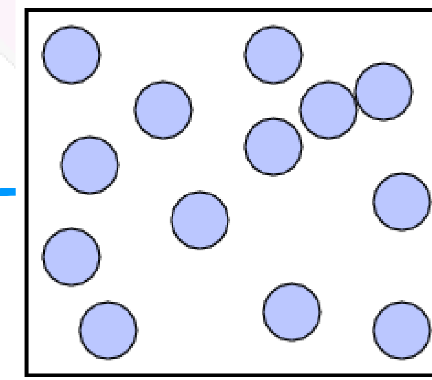
$$E_n(\lambda)\approx E_n^{(0)}+\lambda H'_{nn}+\sum_{k\neq m}\lambda^2\frac{|H'_{nk}|^2}{E_n^{(0)}-E_k^{(0)}}+\ldots$$

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

Hartree-Fock

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

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



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

$$V_H(x) = \sum_m \int dx' \frac{1}{|x - x'|} \left| \langle x' | m^0 \rangle \right|^2$$

$$V_F(x, x') = \sum_m \frac{\langle x | m^0 \rangle \langle m^0 | x' \rangle}{|x - x'|}$$

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

$$\langle x_1 \dots x_N|\Phi_0\rangle \approx \sum_{Permutations} (-1)^P \langle x_i|n\rangle$$

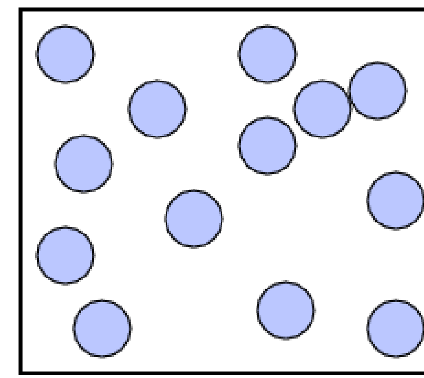
$$\Downarrow$$

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

Hartree-Fock via Variational Methods

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

$$\delta L[\{\chi_n\}] = 0 \qquad \chi_n(x) \equiv \langle x | n \rangle$$

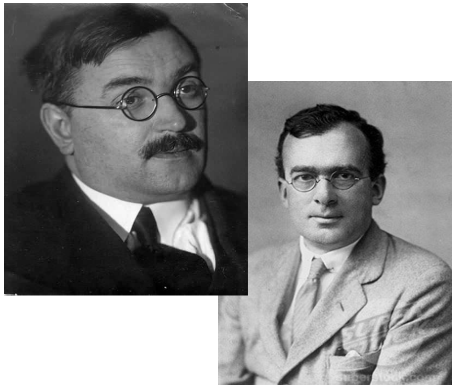


$$h(x)\chi_n(x) + V_H(x)\chi_n(x) - \sum_m \int dx' \, V_F(x,x')\chi_m(x') = \epsilon_n^{HF} \chi_n(x)$$

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

$$V_F(x,x') = \sum_m \frac{\langle x | m \rangle \langle m | x' \rangle}{|x-x'|}$$

Hartree-Fock: take home messages



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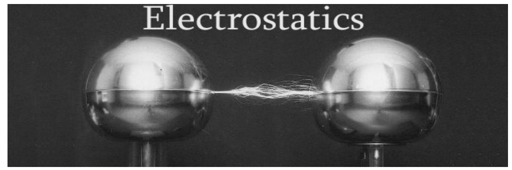

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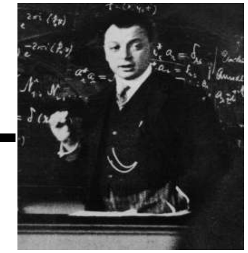

HF is just the sum of electrostatic and exclusion principle

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

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)

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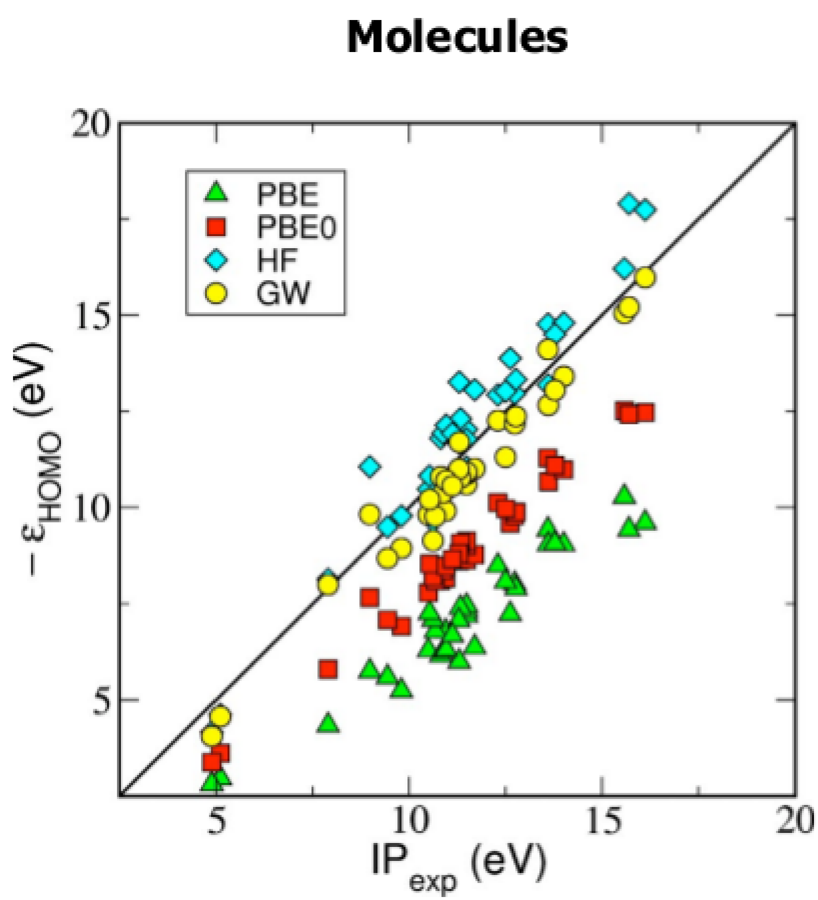
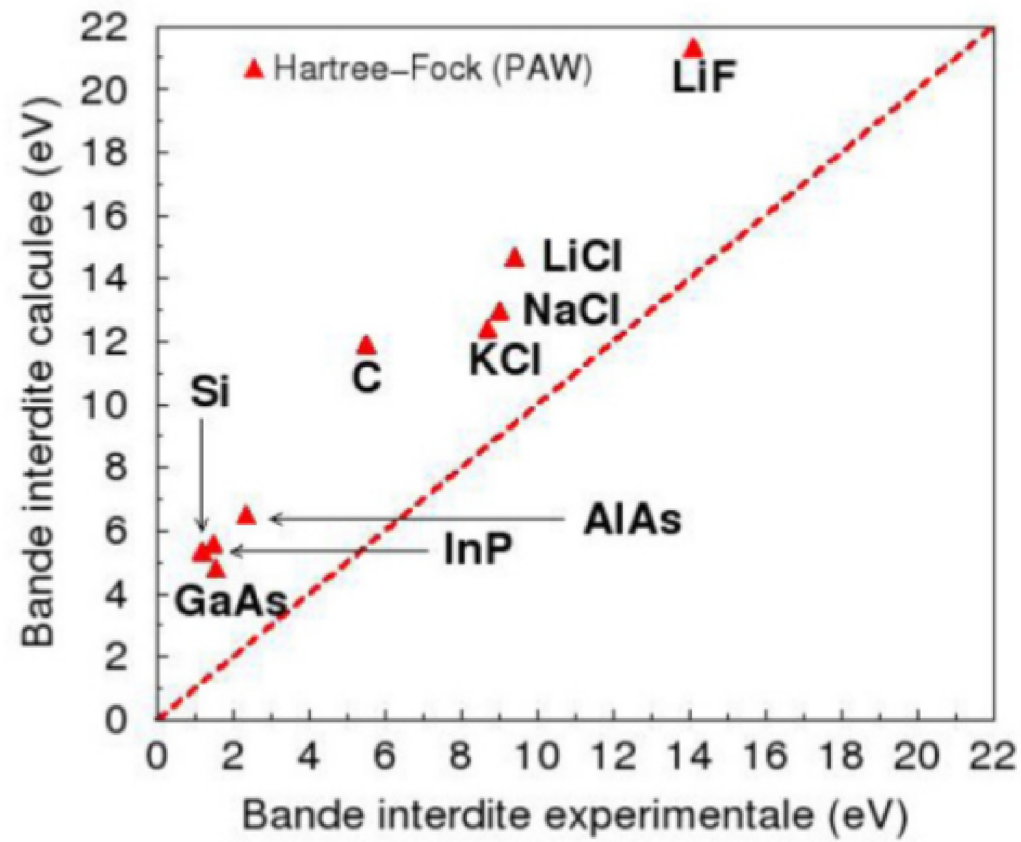
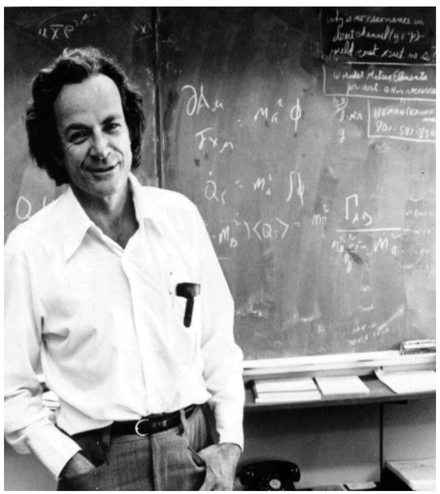
Hartree-Fock: take home message



C. Rostgaard, K. W. Jacobsen, and K. S. Thygesen, PRB **81**, 085103 (2010)



Hartree Fock lacks of CORRELATION



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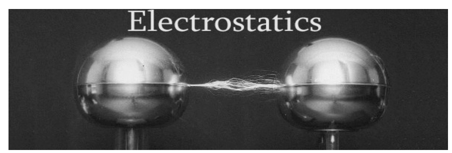

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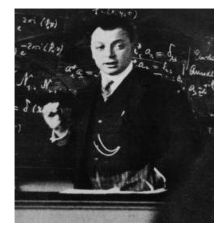

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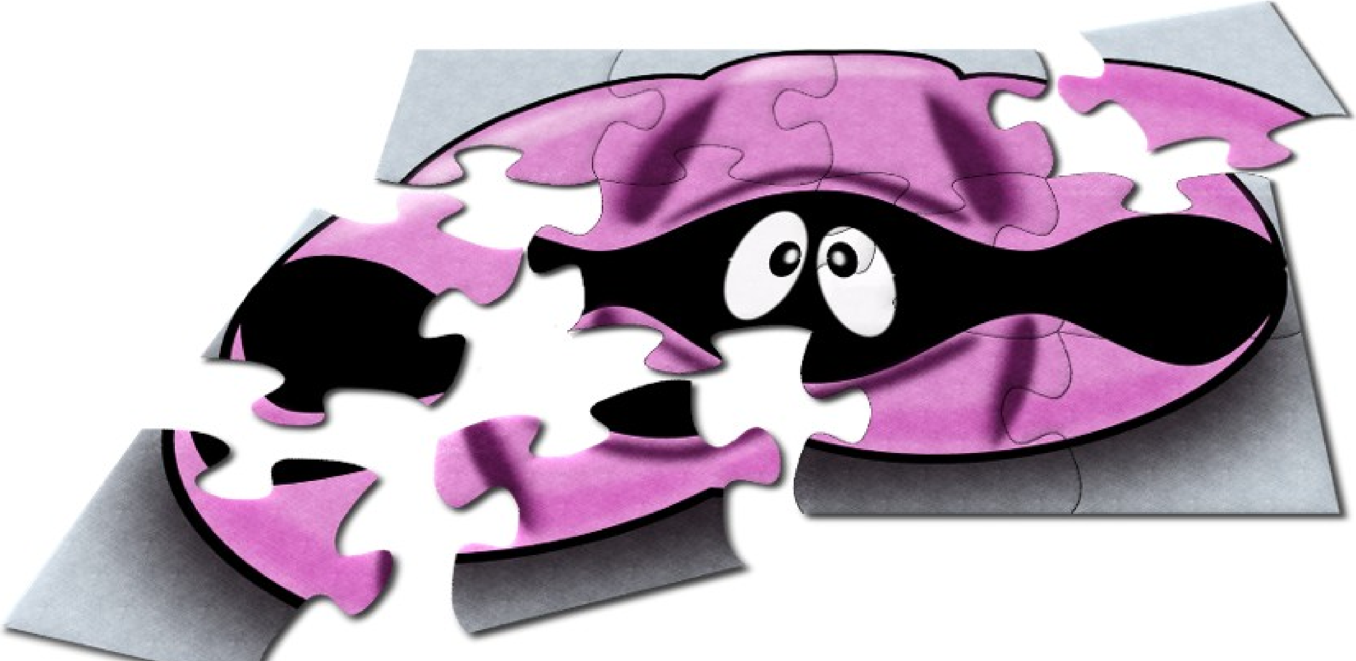

1. Many-body perturbation theory calculations using the yambo code
Journal of Physics: Condensed Matter 31, 325902 (2019)
2. Yambo: an ab initio tool for excited state calculations
Comp. Phys. Comm. 144, 180 (2009)

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