Quantum mechanics for many-particle systems

A short story

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Second quantization

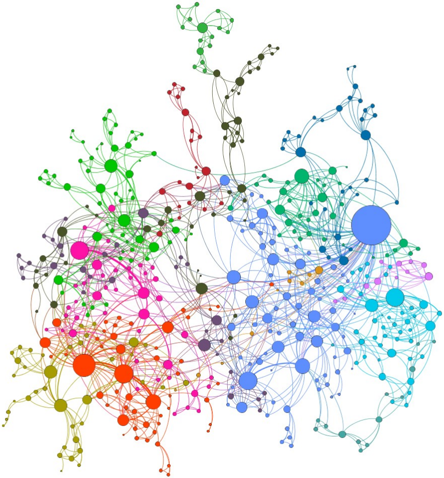

Figure:
https://shoptr3.magmamusicfestival.com/content?c=many+body+physicsid=32

Second quantization

Useful tool for treating systems composed of a large number of particles.

Introduction

Creation and annihilation operators

Second quantization is quantum mechanics.

Second quantization

Why?

Antisymmetry principle

We have satisfaced this principle using Slater determinants.

We transfer the antisymmetry property of the wave function onto the algebraic properties of creation and annihilation operators [1].

How can I transfer this property?

Define:

Creation operator $a_i^\dagger$ for each particle in the single-particle state ϕ_i

$$a_i^\dagger|\phi_\alpha \dots \phi_\gamma\rangle = |\phi_i\phi_\alpha \dots \phi_\gamma\rangle$$

Second quantization

Rules

$$a_i^\dagger a_j^\dagger |\phi_\alpha \dots \phi_\gamma\rangle = |\phi_i \phi_j \phi_\alpha \dots \phi_\gamma\rangle$$

$$a_j^\dagger a_i^\dagger |\phi_\alpha \dots \phi_\gamma\rangle = |\phi_j \phi_i \phi_\alpha \dots \phi_\gamma\rangle = -|\phi_i \phi_j \phi_\alpha \dots \phi_\gamma\rangle$$

The last equation it's associated with antisymmetry property of Slater determinant.
If we sum

$$\left(a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger\right) |\phi_\alpha \dots \phi_\gamma\rangle = 0$$

$$a_i^\dagger a_j^\dagger + a_j^\dagger a_i^\dagger = \{a_i^\dagger, a_j^\dagger\} = 0 \qquad \text{Anticommutator}$$

Pauli exclusion principle

$$a_i^\dagger a_i^\dagger |\phi_\alpha \dots \phi_\gamma\rangle = a_i^\dagger |\phi_i \phi_j \phi_\alpha \dots \phi_\gamma\rangle = 0$$

Second quantization

The way to define annihilation operator is similar, a_i, we're going to considerate as the adjoint of the creation operator

$$(a_i^\dagger)^\dagger = a_i$$

$$a_i|\phi_i\phi_\alpha\ldots\phi_\gamma\rangle = |\phi_\alpha\ldots\phi_\gamma\rangle$$

Rule

$$a_i|\phi_\alpha\phi_\beta\phi_i\rangle = -a_i|\phi_i\phi_\beta\phi_\alpha\rangle = |\phi_\alpha\phi_\beta\rangle$$

Same the creation operator

$$a_ia_j + a_ja_i = \{a_i, a_j\} = 0 \qquad \text{Anticommutator}$$

Combining both operators

$$a_ia_j^\dagger + a_j^\dagger a_i = \{a_i, a_j^\dagger\} = \delta_{ij} = \begin{cases} 1, i = j \\ 0, i \neq j \end{cases}$$

Second quantization

One-body operator

$$\hat{H}_0 = \sum_i \hat{h}_0(x_i)$$

Antisymmetric n particle Slater determinant

$$\Phi(x_1, x_2, \ldots, x_n, \alpha_1, \alpha_2, \ldots, \alpha_n) = \frac{1}{\sqrt{n!}} \sum_p (-1)^p \hat{P} \psi_{\alpha_1}(x_1) \psi_{\alpha_2}(x_2) \ldots \psi_{\alpha_n}(x_n)$$

We can express

$$\hat{h}_0(x_i) \psi_{\alpha_i}(x_i) = \sum_{\alpha'_k} \psi_{\alpha'_k}(x_i) \langle \alpha'_k | \hat{h}_0 | \alpha_k \rangle$$

$$\sum_i \hat{h}_0(x_i) \psi_{\alpha_1}(x_1) \psi_{\alpha_2}(x_2) \ldots \psi_{\alpha_n}(x_n) =$$
$$= \sum_{\alpha'_1} \langle \alpha'_1 | \hat{h}_0 | \alpha_1 \rangle \psi_{\alpha'_1}(x_1) \psi_{\alpha_2}(x_2) \ldots \psi_{\alpha_n}(x_n) + \ldots +$$
$$+ \sum_{\alpha'_n} \langle \alpha'_n | \hat{h}_0 | \alpha_n \rangle \psi_{\alpha_1}(x_1) \psi_{\alpha_2}(x_2) \ldots \psi_{\alpha'_n}(x_n)$$

Second quantization

$$\sum_i \hat{h}_0(x_i)\psi_{\alpha_1}(x_2)\psi_{\alpha_2}(x_1)\ldots\psi_{\alpha_n}(x_n) =$$

$$= \sum_{\alpha_1'}\langle\alpha_1'|\hat{h}_0|\alpha_1\rangle\psi_{\alpha_1'}(x_2)\psi_{\alpha_2}(x_1)\ldots\psi_{\alpha_n}(x_n) + \ldots +$$

$$+ \sum_{\alpha_n'}\langle\alpha_n'|\hat{h}_0|\alpha_n\rangle\psi_{\alpha_1}(x_2)\psi_{\alpha_2}(x_1)\ldots\psi_{\alpha_n'}(x_n)$$

Considering all the permutations, we can write

$$\hat{H}_0|\alpha_1,\alpha_2,\ldots,\alpha_n\rangle = \sum_{\alpha_1'}\langle\alpha_1'|\hat{h}_0|\alpha_1\rangle|\alpha_1',\alpha_2,\ldots,\alpha_n\rangle +$$

$$+ \sum_{\alpha_2'}\langle\alpha_2'|\hat{h}_0|\alpha_2\rangle|\alpha_1,\alpha_2',\ldots,\alpha_n\rangle + \ldots + \sum_{\alpha_n'}\langle\alpha_n'|\hat{h}_0|\alpha_n\rangle|\alpha_1,\alpha_2,\ldots,\alpha_n'\rangle$$

in second quantization form,

$$|\alpha_1,\alpha_2,\ldots,\alpha_k',\ldots,\alpha_n\rangle = a^\dagger_{\alpha_k'}a_{\alpha_k}|\alpha_1,\alpha_2,\ldots,\alpha_k,\ldots,\alpha_n\rangle$$

Second quantization

$$\hat{H}_0|\alpha_1,\alpha_2,\ldots,\alpha_n\rangle = \sum_{\alpha_1'}\langle\alpha_1'|\hat{h}_0|\alpha_1\rangle a^\dagger_{\alpha_1'} a_{\alpha_1}|\alpha_1,\alpha_2,\ldots,\alpha_n\rangle +$$

$$+\sum_{\alpha_2'}\langle\alpha_2'|\hat{h}_0|\alpha_2\rangle a^\dagger_{\alpha_2'} a_{\alpha_2}|\alpha_1,\alpha_2,\ldots,\alpha_n\rangle + \ldots +$$

$$+\sum_{\alpha_n'}\langle\alpha_n'|\hat{h}_0|\alpha_n\rangle a^\dagger_{\alpha_n'} a_{\alpha_n}|\alpha_1,\alpha_2,\ldots,\alpha_n\rangle = \sum_{\alpha\beta}\langle\alpha|\hat{h}_0|\beta\rangle a^\dagger_\alpha a_\beta|\alpha_1,\alpha_2,\ldots,\alpha_n\rangle$$

$$\hat{H}_0 = \sum_{\alpha\beta}\langle\alpha|\hat{h}_0|\beta\rangle a^\dagger_\alpha a_\beta$$

Two-body operator

$$\hat{H}_I = \sum_{i<j} V(x_i,x_j)$$

$$V(x_i,x_j)\psi_{\alpha_k}(x_i)\psi_{\alpha_l}(x_j) = \sum_{\alpha_k'\alpha_l'}\psi_{\alpha_k'}(x_i)\psi_{\alpha_l'}(x_j)\langle\alpha_k'\alpha_l'|\hat{v}|\alpha_k\alpha_l\rangle$$

Second quantization

$$\sum_{i<j} V(x_i, x_j)\psi_{\alpha_1}(x_1)\psi_{\alpha_2}(x_2)\ldots\psi_{\alpha_n}(x_n) =$$

$$= \sum_{\alpha_1'\alpha_2'} \langle\alpha_1'\alpha_2'|\hat{v}|\alpha_1\alpha_2\rangle\psi_{\alpha_1'}(x_1)\psi_{\alpha_2'}(x_2)\ldots\psi_{\alpha_n}(x_n) + \ldots +$$

$$+ \sum_{\alpha_1'\alpha_n'} \langle\alpha_1'\alpha_n'|\hat{v}|\alpha_1\alpha_n\rangle\psi_{\alpha_1'}(x_1)\psi_{\alpha_2}(x_2)\ldots\psi_{\alpha_n'}(x_n) + \ldots +$$

$$+ \sum_{\alpha_2'\alpha_n'} \langle\alpha_2'\alpha_n'|\hat{v}|\alpha_2\alpha_n\rangle\psi_{\alpha_1}(x_1)\psi_{\alpha_2'}(x_2)\ldots\psi_{\alpha_n'}(x_n) + \ldots$$

Considering all the distinct pairs, we can write

$$\hat{H}_I|\alpha_1, \alpha_2, \ldots, \alpha_n\rangle = \sum_{\alpha_1'\alpha_2'} \langle\alpha_1'\alpha_2'|\hat{v}|\alpha_1\alpha_2\rangle|\alpha_1', \alpha_2', \ldots, \alpha_n\rangle + \ldots +$$

$$+ \sum_{\alpha_1'\alpha_n'} \langle\alpha_1'\alpha_n'|\hat{v}|\alpha_1\alpha_n\rangle|\alpha_1', \alpha_2, \ldots, \alpha_n'\rangle + \ldots +$$

Second quantization

$$+\sum_{\alpha_2'\alpha_n'}\langle\alpha_2'\alpha_n'|\hat{v}|\alpha_2\alpha_n\rangle|\alpha_1,\alpha_2',\ldots,\alpha_n'\rangle+\ldots$$

in second quantization form,

$$|\alpha_1,\ldots,\alpha_k',\ldots,\alpha_l',\ldots,\alpha_n\rangle = a^\dagger_{\alpha_k'}a^\dagger_{\alpha_l'}a_{\alpha_k}a_{\alpha_l}|\alpha_1,\alpha_2,\ldots,\alpha_k,\ldots,\alpha_l,\ldots,\alpha_n\rangle$$

$$\hat{H}_I|\alpha_1,\alpha_2,\ldots,\alpha_n\rangle = \sum_{\alpha_1'\alpha_2'}\langle\alpha_1'\alpha_2'|\hat{v}|\alpha_1\alpha_2\rangle a^\dagger_{\alpha_1'}a^\dagger_{\alpha_2'}a_{\alpha_1}a_{\alpha_2}|\alpha_1,\alpha_2,\ldots,\alpha_n\rangle+\ldots+$$

$$+\sum_{\alpha_1'\alpha_n'}\langle\alpha_1'\alpha_n'|\hat{v}|\alpha_1\alpha_n\rangle a^\dagger_{\alpha_1'}a^\dagger_{\alpha_n'}a_{\alpha_1}a_{\alpha_n}|\alpha_1,\alpha_2,\ldots,\alpha_n\rangle+\ldots+$$

$$+\sum_{\alpha_2'\alpha_n'}\langle\alpha_2'\alpha_n'|\hat{v}|\alpha_2\alpha_n\rangle a^\dagger_{\alpha_2'}a^\dagger_{\alpha_n'}a_{\alpha_2}a_{\alpha_n}|\alpha_1,\alpha_2,\ldots,\alpha_n\rangle+\ldots$$

Second quantization

$$= \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta|\hat{v}|\gamma\delta\rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma |\alpha_1, \alpha_2, \ldots, \alpha_n\rangle$$

$$\hat{H}_I = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} \langle \alpha\beta|\hat{v}|\gamma\delta\rangle a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma$$

Wick's theorem

It is a powerful tool to solve vacuum expectation values.

Normal product (Normal-ordered product)

Defined as the rearranged product of operators such that all creation operators are to the left of all annihilation operators [2].

$$n[\hat{A}\hat{B}\hat{C}\ldots] = (-1)^{\sigma(\hat{P})} a^\dagger b^\dagger \ldots uv$$

$$a^\dagger b^\dagger \ldots uv = \hat{P}(\hat{A}\hat{B}\hat{C}\ldots)$$

Second quantization

$$\langle 0|\hat{X}\hat{Y}\hat{Z}\ldots\hat{W}|0\rangle \longrightarrow \hat{X}\hat{Y}\hat{Z}\ldots\hat{W}$$

$$\hat{X}\hat{Y}\hat{Z}\ldots\hat{W} = \sum_{(1)} N[XYZ\ldots W] + \sum_{(2)} N[XYZ\ldots \quad \ldots W] + \ldots +$$

$$+ \sum_{\left(\frac{N}{2}\right)} N[XYZ\ldots \quad \ldots \quad W]$$

Result

$$\langle 0|\hat{X}\hat{Y}\hat{Z}\ldots\hat{W}|0\rangle = \langle 0| \sum_{\left(\frac{N}{2}\right)} N[XYZ\ldots \quad \ldots \quad W]|0\rangle$$

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Hartree-Fock theory

Ground state energy by E_0

$$E_0 \leq E[\Phi] = \int \Phi^* \hat{H} \Phi d\tau$$

we assume that Φ is normalized. Slater determinant:

$$\Psi(x_1, x_2, \ldots, x_n, \alpha, \beta, \ldots, \nu) = \frac{1}{\sqrt{N!}} \sum_p (-1)^p \hat{P} \underbrace{\psi_\alpha(x_1)\psi_\beta(x_2)\ldots\psi_\nu(x_N)}_{\Phi_H}$$

we written

$$E[\Phi] = \sum_{\mu=1}^{N} \int \psi_\mu^*(x_i) \hat{h}_0 \psi_\mu(x_i) dx_i + \frac{1}{2} \sum_{\mu=1}^{N} \sum_{\nu=1}^{N} \left[\int \psi_\mu^*(x_i) \psi_\nu^*(x_j) \hat{v}(r_{ij}) \psi_\mu(x_i) \times \right.$$

$$\left. \times \psi_\nu(x_j) dx_i dx_j - \int \psi_\mu^*(x_j) \psi_\nu^*(x_i) \hat{v}(r_{ij}) \psi_\mu(x_i) \psi_\nu(x_j) dx_i dx_j \right]$$

Hartree-Fock theory

Compact form

$$E[\Phi] = \sum_{\mu}^{N} \langle \mu | \hat{h}_0 | \mu \rangle + \frac{1}{2} \sum_{\mu\nu}^{N} \left[\langle \mu\nu | \hat{v} | \mu\nu \rangle - \langle \nu\mu | \hat{v} | \mu\nu \rangle \right]$$

$$E[\Phi] = \sum_{\mu}^{N} \langle \mu | \hat{h}_0 | \mu \rangle + \frac{1}{2} \sum_{\mu\nu}^{N} \langle \mu\nu | \hat{v} | \mu\nu \rangle_{AS}$$

we can write the variational equation with the Lagrange multipliers

$$\delta \left(E[\Phi] - \sum_{\mu\nu}^{N} \epsilon_{\mu\nu} \int \psi_{\mu}^{*} \psi_{\mu} \right) = 0$$

Variation with respect ψ_{μ}^{*}

$$\left(\hat{h}_0 + \sum_{\nu=1}^{N} \int \psi_{\nu}^{*}(x_j) \hat{v}(r_{ij}) \psi_{\nu}(x_j) dx_j \right) \psi_{\mu}(x_i) -$$

$$- \left(\int \psi_{\nu}^{*}(x_j) \hat{v}(r_{ij}) \psi_{\mu}(x_j) dx_j \right) \psi_{\nu}(x_i) = \epsilon_{\mu} \psi_{\mu}(x_i)$$

Varying the coefficients

New basis

$$\psi_p(x) = \sum_{\lambda} C_{p\lambda}\phi_{\lambda}(x)$$

$$\Psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} det \begin{vmatrix} \psi_p(x_1) & \psi_p(x_2) & \dots & \psi_p(x_N) \\ \psi_p(x_1) & \psi_p(x_2) & \dots & \psi_p(x_N) \\ \vdots & \vdots & \dots & \vdots \\ \psi_p(x_1) & \psi_p(x_2) & \dots & \psi_p(x_N) \end{vmatrix}$$

$$= \frac{1}{\sqrt{N!}} det \begin{vmatrix} \sum_\lambda C_{p\lambda}\phi_\lambda(x_1) & \sum_\lambda C_{p\lambda}\phi_\lambda(x_2) & \dots & \sum_\lambda C_{p\lambda}\phi_\lambda(x_N) \\ \sum_\lambda C_{p\lambda}\phi_\lambda(x_1) & \sum_\lambda C_{p\lambda}\phi_\lambda(x_2) & \dots & \sum_\lambda C_{p\lambda}\phi_\lambda(x_N) \\ \vdots & \vdots & \dots & \vdots \\ \sum_\lambda C_{p\lambda}\phi_\lambda(x_1) & \sum_\lambda C_{p\lambda}\phi_\lambda(x_2) & \dots & \sum_\lambda C_{p\lambda}\phi_\lambda(x_N) \end{vmatrix}$$

Hartree-Fock theory

Energy functional in terms of the basis function $\phi_\lambda(r)$

$$E[\Phi] = \sum_{\mu}^{N} \langle \mu | \hat{h}_0 | \mu \rangle + \frac{1}{2} \sum_{\mu\nu}^{N} \langle \mu\nu | \hat{v} | \mu\nu \rangle_{AS}$$

we define a new basis

$$E[\Phi^{HF}] = \sum_{i}^{N} \langle i | \hat{h}_0 | i \rangle + \frac{1}{2} \sum_{ij}^{N} \langle ij | \hat{v} | ij \rangle_{AS}$$

$$E[\Phi^{HF}] = \sum_{i=1}^{N} \sum_{\alpha\beta} C^*_{i\alpha} C_{i\beta} \langle \alpha | h | \beta \rangle + \frac{1}{2} \sum_{i,j=1}^{N} \sum_{\alpha\beta\gamma\delta} C^*_{i\alpha} C^*_{j\beta} C_{i\gamma} C_{j\delta} \langle \alpha\beta | v | \gamma\delta \rangle_{AS}$$

$$\langle i | j \rangle = \delta_{ij} = \sum_{\alpha\beta} C^*_{i\alpha} C_{i\beta} \langle \alpha | \beta \rangle = \sum_{\alpha} C^*_{i\alpha} C_{i\alpha}$$

Hartree-Fock theory

Functional

$$F[\Phi^{HF}] = E[\Phi^{HF}] + \sum_{i=1}^{N} \epsilon_i \sum_{\alpha} C^*_{i\alpha} C_{i\alpha}$$

Minimizing with respect to $C^*_{i\alpha}$

$$\frac{d}{dC^*_{i\alpha}} \left[E[\Phi^{HF}] + \sum_{i=1}^{N} \epsilon_i \sum_{\alpha} C^*_{i\alpha} C_{i\alpha} \right] = 0$$

$$\sum_{\beta} C_{i\beta} \langle \alpha | h | \beta \rangle + \sum_{j=1}^{N} \sum_{\beta\gamma\delta} C^*_{j\beta} C_{i\gamma} C_{j\delta} \langle \alpha\beta | v | \gamma\delta \rangle_{AS} = \epsilon_i^{HF} C_{i\alpha}$$

changing dummy variables

$$\sum_{\beta} \left\{ \langle \alpha | h | \beta \rangle + \sum_{j=1}^{N} \sum_{\beta\gamma\delta} C^*_{j\gamma} C_{j\delta} \langle \alpha\gamma | v | \beta\delta \rangle_{AS} \right\} C_{i\beta} = \epsilon_i^{HF} C_{i\alpha}$$

Hartree-Fock theory

We can define

$$h_{\alpha\beta}^{HF} = \langle\alpha|h|\beta\rangle + \sum_{j=1}^{N}\sum_{\gamma\delta} C_{j\gamma}^{*} C_{j\delta}\langle\alpha\gamma|v|\beta\delta\rangle_{AS}$$

Hartree-Fock equations

$$\sum_{\beta} h_{\alpha\beta}^{HF} C_{i\beta} = \epsilon_i^{HF} C_{i\alpha}$$

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Full Configuration Interaction (FCI)

Using the determinant formalism

$$\Psi(x_1, x_2, \dots, x_N) = \frac{1}{\sqrt{N!}} det \begin{vmatrix} \phi_1(x_1) & \phi_1(x_2) & \dots & \phi_1(x_N) \\ \phi_2(x_1) & \phi_2(x_2) & \dots & \phi_2(x_N) \\ \vdots & \vdots & \dots & \vdots \\ \phi_N(x_1) & \phi_N(x_2) & \dots & \phi_N(x_N) \end{vmatrix}$$

Product wavefunction $+$ antisymmetry $=$ Determinant

Slater dterminant follow the Pauli principle.
We define the ground state

$$|\Phi_0\rangle = \left(\prod_{i \le F} a_i^\dagger \right) |0\rangle$$

Full Configuration Interaction (FCI)

Particle-Hole formalism

$$
\begin{aligned}
&|\Phi_i^a\rangle = a_a^\dagger a_i|\Phi_0\rangle \longrightarrow 1p1h \\
&|\Phi_{ij}^{ab}\rangle = a_a^\dagger a_b^\dagger a_i a_j|\Phi_0\rangle \longrightarrow 2p2h \\
&\vdots \\
&|\Phi_{ijk\ldots}^{abc\ldots}\rangle = a_a^\dagger a_b^\dagger a_c^\dagger \ldots a_i a_j a_k|\Phi_0\rangle \longrightarrow NpNh
\end{aligned}
$$

Expanding the exact state function for the ground state

$$
|\Psi_0\rangle = C_0|\Phi_0\rangle + \sum_{ai} C_i^a|\Phi_i^a\rangle + \ldots + \sum_{abcijk\ldots} C_{ijk\ldots}^{abc\ldots}|\Phi_{ijk\ldots}^{abc\ldots}\rangle
$$

We can define the correlation operator

$$
\hat{C} = \sum_{ai} C_i^a a_a^\dagger a_i + \ldots + \sum_{abcijk\ldots} C_{ijk\ldots}^{abc\ldots} a_a^\dagger a_b^\dagger a_c^\dagger \ldots a_i a_j a_k
$$

Full Configuration Interaction (FCI)

$$C_0 = 1$$

$$|\Psi_0\rangle = (1 + \hat{C})|\Phi_0\rangle$$

in particle-hole terms

$$|\Psi_0\rangle = \sum_{ph} C_h^p \Phi_h^p = \sum_{ph} C_h^p \hat{A}_h^p |\Phi_0\rangle$$

unit normalization

$$\langle\Psi_0|\Psi_0\rangle = \sum_{ph} |C_h^p|^2 = 1$$

energy

$$E = \langle\Psi_0|\hat{H}|\Psi_0\rangle = \sum_{pp'hh'} C_h^{*p} \langle\Phi_h^p|\hat{H}|\Phi_{h'}^{p'}\rangle C_{h'}^{p'}$$

Diagonalization, finding the variational minimum

$$F = \langle\Psi_0|\hat{H}|\Psi_0\rangle - \lambda\langle\Psi_0|\Psi_0\rangle$$

Full Configuration Interaction (FCI)

Minimization

$$\delta[\langle\Psi_0|\hat{H}|\Psi_0\rangle - \lambda\langle\Psi_0|\Psi_0\rangle] = 0$$

$$\delta[\sum_{pp'hh'} C_h^{*p}\langle\Phi_h^p|\hat{H}|\Phi_{h'}^{p'}\rangle C_{h'}^{p'} - \lambda\sum_{ph} C_h^{*p} C_{h'}^{p'}] = 0$$

$$\sum_{p'h'}\left\{\delta C_h^{*p}\langle\Phi_h^p|\hat{H}|\Phi_{h'}^{p'}\rangle C_{h'}^{p'} - \lambda\delta C_h^{*p} C_{h'}^{p'}\right\} = 0$$

$$\sum_{p'h'}\langle\Phi_h^p|\hat{H}|\Phi_{h'}^{p'}\rangle C_{h'}^{p'} - \lambda C_h^p = 0$$

multiply by C_h^{*p} and sum over ph

$$\sum_{pp'hh'} C_h^{*p}\langle\Phi_h^p|\hat{H}|\Phi_{h'}^{p'}\rangle C_{h'}^{p'} - \lambda\sum_{ph}|C_h^p|^2 = 0$$

therefore

$$\lambda = E$$

Full Configuration Interaction (FCI)

FCI equations

$$\sum_{p'h'} \langle \Phi_h^p | \hat{H} | \Phi_{h'}^{p'} \rangle C_{h'}^{p'} = E C_h^p$$

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Many-body perturbation theory

Ground state of the system and expand

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{m=1}^{\infty} C_m |\Psi_m\rangle$$

Assume that true ground state (unperturbed hamiltonian)

$$\hat{H}_0 |\Phi_0\rangle = W_0 |\Phi_0\rangle$$

$|\Psi_0\rangle$ is a wave function unknow, not normalized. We used an intermediate normalization

$$\langle \Phi_0 | \Psi_0 \rangle = 1$$
$$\langle \Phi_0 | \Phi_0 \rangle = 1$$

Schrödinger equation

$$\hat{H} |\Psi_0\rangle = E |\Psi_0\rangle$$
$$\langle \Phi_0 | \hat{H} | \Psi_0 \rangle = \langle \Phi_0 | E | \Psi_0 \rangle = E$$

Many-body perturbation theory

and

$$\langle \Psi_0 | \hat{H}_0 | \Phi_0 \rangle = \langle \Psi_0 | W_0 | \Phi_0 \rangle = W_0$$

correlation energy

$$\langle \Phi_0 | \hat{H}_I | \Psi_0 \rangle = E - W_0 = \Delta E$$

we have assumed that our model space

$$\hat{P} = |\Phi_0\rangle\langle\Phi_0|$$

$$\hat{Q} = \sum_{m=1}^{\infty} |\Phi_m\rangle\langle\Phi_m|$$

rewrite the exact wave function

$$|\Psi_0\rangle = (\hat{P} + \hat{Q})|\Psi_0\rangle = |\Phi_0\rangle + \hat{Q}|\Psi_0\rangle$$

adding and a subtracting $\omega|\Psi_0\rangle$ in Schrödinger equation

Many-body perturbation theory

$$(\omega - \hat{H}_0)|\Psi_0\rangle = (\omega - E + \hat{H}_I)|\Psi_0\rangle$$

$$|\Psi_0\rangle = \frac{1}{\omega - \hat{H}_0}(\omega - E + \hat{H}_I)|\Psi_0\rangle$$

multiplying by $\hat{Q}$

$$\hat{Q}|\Psi_0\rangle = \frac{\hat{Q}}{\omega - \hat{H}_0}(\omega - E + \hat{H}_I)|\Psi_0\rangle$$

therefore, we can define

$$|\Psi_0\rangle = |\Phi_0\rangle + \frac{\hat{Q}}{\omega - \hat{H}_0}(\omega - E + \hat{H}_I)|\Psi_0\rangle$$

E and $|\Psi_0\rangle$ are unknow

Many-body perturbation theory

$$|\Psi_0\rangle = \sum_{i=0}^{\infty} \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} (\omega - E + \hat{H}_I) \right\}^i |\Phi_0\rangle$$

$$\Delta E = \sum_{i=0}^{\infty} \langle \Phi_0 | \hat{H}_I \left\{ \frac{\hat{Q}}{\omega - \hat{H}_0} (\omega - E + \hat{H}_I) \right\}^i |\Phi_0\rangle$$

In Rayleigh-Schrödinger perturbation theory we set $\omega = W_0$

$$\Delta E = \langle \Phi_0 | \left(\hat{H}_I + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} (\hat{H}_I - \Delta E) + \right.$$
$$\left. + \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} (\hat{H}_I - \Delta E) \frac{\hat{Q}}{W_0 - \hat{H}_0} (\hat{H}_I - \Delta E) + \dots \right) |\Phi_0\rangle$$

Since $[\hat{Q}, \hat{H}_0] = 0$

$$\hat{Q} \Delta E |\Phi_0\rangle = \hat{Q} \Delta E |\hat{Q} \Phi_0\rangle = 0$$

Many-body perturbation theory

$$\Delta E = \langle\Phi_0|\left(\hat{H}_I + \hat{H}_I\frac{\hat{Q}}{W_0-\hat{H}_0}\hat{H}_I + \hat{H}_I\frac{\hat{Q}}{W_0-\hat{H}_0}(\hat{H}_I-\Delta E)\frac{\hat{Q}}{W_0-\hat{H}_0}\hat{H}_I + \dots\right.$$

$$\Delta E = \sum_{i=1}^{\infty}\Delta E^{(i)}$$

$$\Delta E^{(1)} = \langle\Phi_0|\hat{H}_I|\Phi_0\rangle$$

$$\Delta E^{(2)} = \langle\Phi_0|\hat{H}_I\frac{\hat{Q}}{W_0-\hat{H}_0}\hat{H}_I|\Phi_0\rangle$$

$$\Delta E^{(3)} = \langle\Phi_0|\hat{H}_I\frac{\hat{Q}}{W_0-\hat{H}_0}\hat{H}_I\frac{\hat{Q}}{W_0-\hat{H}_0}\hat{H}_I|\Phi_0\rangle - \langle\Phi_0|\hat{H}_I\frac{\hat{Q}}{W_0-\hat{H}_0}\Delta E\frac{\hat{Q}}{W_0-\hat{H}_0}$$

Many-body perturbation theory

$$\Delta E^{(3)} = \langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I | \Phi_0 \rangle -$$

$$- \langle \Phi_0 | \hat{H}_I \frac{\hat{Q}}{W_0 - \hat{H}_0} \langle \Phi_0 | \hat{H}_I | \Phi_0 \rangle \frac{\hat{Q}}{W_0 - \hat{H}_0} \hat{H}_I | \Phi_0 \rangle$$

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