Select/Special Topics from
'Theory of Atomic Collisions and Spectroscopy'

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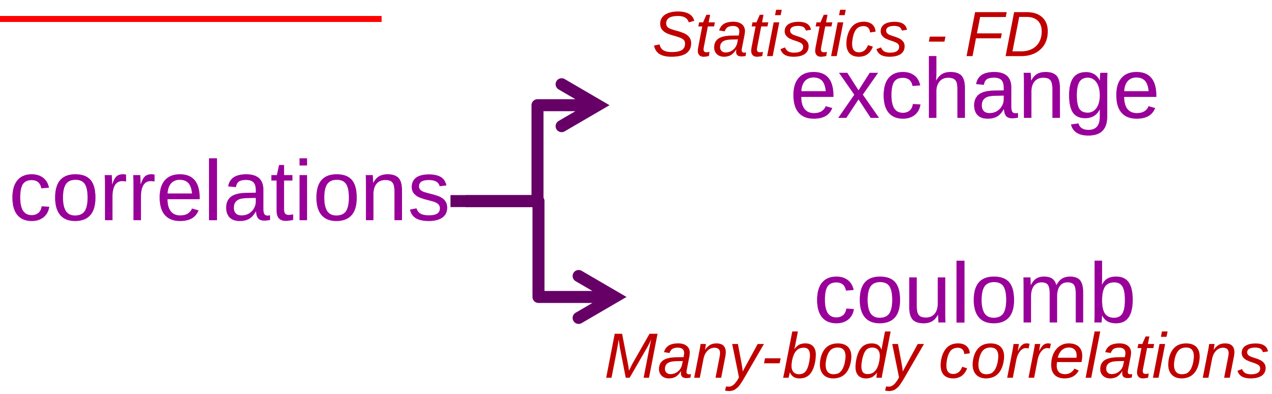
Unit 2 Lecture Number 13

Many-body theory,
electron correlations,
Feynman-Goldstone diagrams

Recall: STiAP Unit 4 HF SCF

Problems of current interest in the physics of ***atoms, molecules and other forms of condensed matter*** require a thorough understanding of electron interactions and electron correlations.



How does STATISTICS enter classical mechanics, and how does it enter quantum mechanics?

Equipartition Theorem: Each degree of freedom in the classical expression for the Hamiltonian contributes $\frac{1}{2}k_B T$ to the AVERAGE energy.

In Quantum Theory, STATISTICS enters through TWO channels:

[1] Uncertainty Principle

[2] "SPIN"; Identity of Particles

$$\hat{I}\ \left\{\hat{I}\ \Psi(q_1,q_2)\right\} = \Psi(q_1,q_2)$$

Interchange operator acting TWICE on a 'geminal' wavefunction

$$\hat{I}\ \Psi(q_1,q_2) = e^{i\alpha}\Psi(q_2,q_1)$$

$$e^{i2\alpha} = 1,\quad \mathrm{e}^{i\alpha} = \pm 1$$

$$\alpha = 0 \quad \text{or} \quad \pi$$

Bosons or Fermions

$$\hat{I}\ \Psi(q_1,q_2) = \pm\Psi(q_2,q_1)$$

$$\text{Fermions: spin } \frac{1}{2},\frac{3}{2},\frac{5}{2},\frac{7}{2}......$$

$$\text{Bosons : spin } 0,1,2,3,4,......$$

$$u_\alpha(q_i) = \langle i\,|\,\alpha\rangle = \langle \vec{r}_i,\zeta_i\,|\,n_\alpha,l_\alpha,m_{l_\alpha},m_{s_\alpha}\rangle$$

$$\hat{I}\ \Psi(q_1, q_2) = e^{i\alpha}\Psi(q_1, q_2)$$

$$e^{i2\alpha} = 1, \quad e^{i\alpha} = \pm 1$$

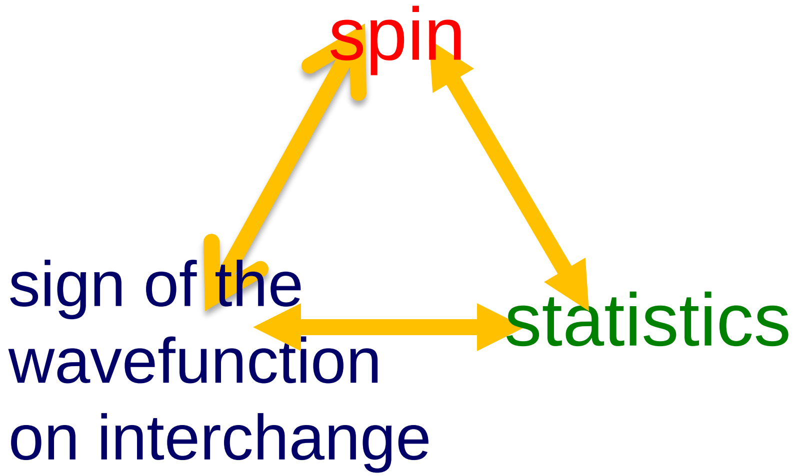
$$\alpha = 0 \quad \text{or} \quad \pi$$

Bosons or Fermions

$$\hat{I}\ \Psi(q_1, q_2) = \pm\Psi(q_1, q_2)$$

Fermions: spin $\frac{1}{2}, \frac{3}{2}, \frac{5}{2}, \frac{7}{2}$......

Bosons : spin $0, 1, 2, 3, 4,$......



"RELATION BETWEEN SPIN & STATISTICS IS APPARENT, BUT HARD TO UNDERSTAND."

- Tomonaga

"…. a rule which can be stated very simply, but … The explanation is down deep in relativistic quantum mechanics." *- Feynman* *Vol.3 p4-3*

For electrons:

$$\widehat{I}\ \Psi(q_1, q_2) = \Psi(q_2, q_1) = -\Psi(q_1, q_2)$$

$$separability\ in\ 'two-electron'\ coordinates:$$

$$\Psi(q_1, q_2) = N\left[u_1(q_1)u_2(q_2) - u_1(q_2)u_2(q_1)\right]$$

$$\boxed{u_\alpha(q_i) = \langle i \mid \alpha \rangle = \langle \vec{r}_i, \zeta_i \mid n_\alpha, l_\alpha, m_{l_\alpha}, m_{s_\alpha} \rangle}$$

Reconcile!

- indistinguishable
- ‘elementary particles’

$$\Psi(q_1,q_2)=N\left[u_1(q_1)u_2(q_2)-u_1(q_2)u_2(q_1)\right]$$

$$=\frac{1}{\sqrt{2}}\begin{vmatrix}u_1(q_1) & u_1(q_2)\\ u_2(q_1) & u_2(q_2)\end{vmatrix}$$

Rows: occupied single particle states (labeled by a set of 4 quantum numbers) in the many-electron system.

Columns: set of (space, spin) coordinates

John C. SLATER DETERMINANT

- Pauli exclusion principle
- Antisymmetry of the wavefunction

Elements of the SLATER DETERMINANT

One-electron SPIN-ORBITALS

$$u_\alpha(q_i) = \langle i \mid \alpha \rangle$$

$$= \langle \vec{r}_i, \zeta_i \mid n_\alpha, l_\alpha, m_{l_\alpha}, m_{s_\alpha} \rangle$$

$$u_\alpha(q_i) = \langle \vec{r}_i \mid n_\alpha, l_\alpha, m_{l_\alpha} \rangle \langle \zeta_i \mid m_{s_\alpha} \rangle$$

Spin part

Orbital part

$$u_\alpha(q_i) = \psi_{n_\alpha, l_\alpha, m_{l_\alpha}}(\vec{r}_i)\, \chi_{m_{s_\alpha}}(\zeta_i)$$

SLATER DETERMINANT

i^{th} column

$$\psi^{(N)} = \frac{1}{\sqrt{N!}} \begin{vmatrix} u_1(1) & .. & .. & .. & u_1(q_N) \\ u_2(1) & .. & .. & .. & .. \\ .. & .. & .. & \langle i|\alpha\rangle = u_\alpha(q_i) & \langle q_N|\alpha\rangle \\ .. & .. & .. & .. & .. \\ u_N(1) & .. & .. & .. & u_N(N) \end{vmatrix}$$

α^{th} row

$$u_\alpha(q_i) = \psi_{n_\alpha, l_\alpha, m_{l_\alpha}}(\vec{r}_i)\, \chi_{m_{s_\alpha}}(\zeta_i)$$

Probability amplitude that an electron at space-spin coordinate $q_i \equiv (\vec{r}_i, \zeta_i)$ is in the quantum state $|\alpha\rangle$.

$$|\alpha\rangle \equiv |n_\alpha, l_\alpha, m_{l_\alpha}, m_{s_\alpha}\rangle$$

$$\psi^{(N)}_{1,2,\ldots N}(q_1,..,q_N) = \frac{1}{\sqrt{N!}} \sum_{P=1}^{N!} (-1)^P P \,[u_1(q_1)u_2(q_2)..u_N(q_N)]$$

Antisymmetriser operator $\hat{A}$

The 'Many-Electron' Atom:

$$H^{(N)}\psi^{(N)} = E^{(N)}\psi^{(N)}$$

The problem can be posed formally,

but the very conceptualization of the N-electron problem leads to an immediate 'CATCH-22' situation –

- awkward situation whose solution is ruled out by a constraint intrinsic to the situation.

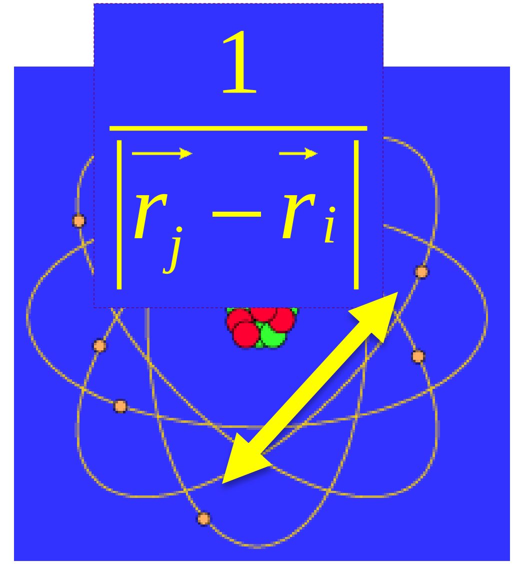
Catch-22 : novel by Joseph Heller.

D.R.Hartree
1897 - 1958
Cambridge, England

$$H^{(N)}\psi^{(N)} = E^{(N)}\psi^{(N)}$$

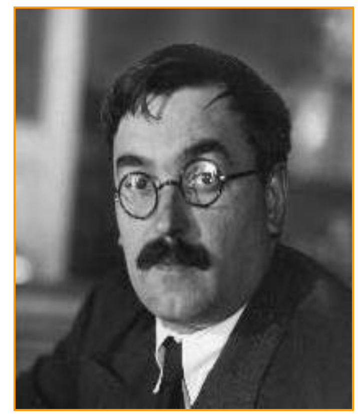
$$H^{(N)} = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^{\,2} - \frac{Z}{r_i}\right) + \sum_{i<j=1}^{N}\frac{1}{r_{ij}}$$

$$H^{(N)}\psi^{(N)} = E^{(N)}\psi^{(N)}$$



$$\frac{1}{\left|\vec{r}_j - \vec{r}_i\right|}$$

Approximate Numerical Solutions



Self- Consistent-Field

V.A.Fock
1898-1974

$$H^{(N)}(q_1,..,q_N)\psi^{(N)}(q_1,..,q_N)=E^{(N)}\psi^{(N)}(q_1,..,q_N)$$

'Exact Solution' ?

"Having no body at all is already too many"

– G. E. Brown

… even ***if*** it were possible to get an exact solution, how much space, ink, storage would be needed to write the solution?

… even ***if*** it were possible to get an exact solution, how much space, ink, storage would be needed to write the solution?

Hartree/ Hermann-Skillman/Johnson:

For N electrons described by only the 3 space

coordinates: 3N variables

Coarse 10-point grid: 10^{3N} numbers to tabulate!

Estimate for N=1, 10, 80… will you?

$q_i = (\vec{r}_i, \zeta_i),$ space and 'spin' coordinate

Approx. Numerical Solutions: Self- Consistent-Field

$$H^{(N)}\psi^{(N)} = E^{(N)}\psi^{(N)}$$ SCF

$$H^{(N)}(q_1, q_2, .., q_N) = \sum_{i=1}^{N}\left(-\frac{1}{2}\nabla_i^{\ 2} - \frac{Z}{r_i}\right) + \sum_{i<j=1}^{N}\frac{1}{r_{ij}}$$

$$= \sum_{i=1}^{N} h_0(q_i) + \frac{1}{2}\sum_{i=1;i\neq j}^{N}\sum_{j=1}^{N}\frac{1}{r_{ij}} \qquad = H_1 + H_2$$

STRATEGY $\delta\langle\psi^{(N)} | H^{(N)} | \psi^{(N)}\rangle = 0$

CONSTRAINTS $\langle i | j\rangle = \delta_{ij}$

We need: $\langle\Psi | \Omega | \Psi\rangle$ with $\Omega = F; \quad \Omega = G$

Two-electron (geminal) state:

$$\psi(q_1, q_2) = \phi(\vec{r}_1, \vec{r}_2)\chi(\zeta_1, \zeta_2)$$

$$\psi(q_2, q_1) = - \psi(q_1, q_2)$$

$$= - \left\{\phi(\vec{r}_1, \vec{r}_2)\chi(\zeta_1, \zeta_2)\right\}$$

$$\psi(q_2, q_1) = \left\{ - \phi(\vec{r}_1, \vec{r}_2)\right\} \chi(\zeta_1, \zeta_2)$$

$$= \phi(\vec{r}_1, \vec{r}_2) \left\{ - \chi(\zeta_1, \zeta_2)\right\}$$

which part, 'space part' or 'spin part',

is antisymmetric, and which is symmetric ?

Two-electron (geminal) state: $\psi(q_1,q_2)=\phi(\vec{r}_1,\vec{r}_2)\chi(\zeta_1,\zeta_2)$

$$\psi(q_2,q_1)=-\psi(q_1,q_2)=-\left\{\phi(\vec{r}_1,\vec{r}_2)\chi(\zeta_1,\zeta_2)\right\}$$

$$\psi(q_2,q_1)=\left\{-\phi(\vec{r}_1,\vec{r}_2)\right\}\chi(\zeta_1,\zeta_2)$$

$$=\phi(\vec{r}_1,\vec{r}_2)\left\{-\chi(\zeta_1,\zeta_2)\right\}$$

$\vec{S}=\vec{s}_1+\vec{s}_2 \quad S=0,1$

$S=0; M_S=0$

$S=1; M_S=-1,0,1$

$\phi(\vec{r}_2,\vec{r}_1)=+\phi(\vec{r}_1,\vec{r}_2)$ and $\chi(\zeta_2,\zeta_1)=-\chi(\zeta_1,\zeta_2)$

Singlet State

or

Triplet State

$\phi(\vec{r}_2,\vec{r}_1)=-\phi(\vec{r}_1,\vec{r}_2)$ and $\chi(\zeta_2,\zeta_1)=+\chi(\zeta_1,\zeta_2)$

"Triplet State is less punished by the coulomb interaction"

- Landau & Lifshitz

$$\left|jm_j\right) = \sum_{m_l=-l}^{l} \sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} \left|m_l m_s\right\rangle \left\langle m_l m_s \right| jm_j \Big)$$

$$\left|m_l m_s\right\rangle = \sum_{j=\left|l-\frac{1}{2}\right|}^{l+\frac{1}{2}} \sum_{m_j=-j}^{j} \left|jm_j\right)\Big(jm_j\Big|m_l m_s\Big\rangle$$

Special/Select Topics
in Atomic Physics

http://nptel.iitm.ac.in/courses/115106057/7

to

http://nptel.iitm.ac.in/courses/115106057/12

$$\left|\alpha\right\rangle = \left|n_\alpha l_\alpha m_{l_\alpha} m_{s_\alpha}\right\rangle$$

or

$$\left|\alpha\right\rangle = \left|n_\alpha l_\alpha j_\alpha m_{j_\alpha}\right\rangle$$

Spherical Harmonic Spinors $\Omega_{j\ell m}$

STiAP Unit 3

$$\Omega_{j\ell m} \overset{\text{definition}}{\underset{\rightarrow}{=}} \sum_{m_{\ell'}=-\ell}^{\ell} \sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} Y_{\ell m_{\ell'}}(\hat{r})\chi_{\frac{1}{2},m_s}(\zeta)\left\langle \ell m_{\ell'}\frac{1}{2}m_s \middle| \left(\ell\frac{1}{2}\right)jm \right\rangle$$

$$\Omega_{j\ell m} = \sum_{m_s=-\frac{1}{2}}^{\frac{1}{2}} Y_{\ell(m_{\ell'}=m-m_s)}(\hat{r})\chi_{\frac{1}{2},m_s}(\zeta)\left\langle \ell,(m_{\ell'}=m-m_s),\frac{1}{2}m_s \middle| \left(\ell\frac{1}{2}\right)jm \right\rangle$$

$$\Omega_{j\ell m} = Y_{\ell\left(m_{\ell'}=m+\frac{1}{2}\right)}(\hat{r})\chi_{\frac{1}{2},m_s=-\frac{1}{2}}(\zeta)\left\langle \ell,\left(m_{\ell'}=m+\frac{1}{2}\right),\frac{1}{2},-\frac{1}{2} \middle| \left(\ell\frac{1}{2}\right)jm \right\rangle$$

$$+$$

$$Y_{\ell\left(m_{\ell'}=m-\frac{1}{2}\right)}(\hat{r})\chi_{\frac{1}{2},\frac{1}{2}}(\zeta)\left\langle \ell,\left(m_{\ell'}=m-\frac{1}{2}\right),\frac{1}{2},\frac{1}{2} \middle| \left(\ell\frac{1}{2}\right)jm \right\rangle$$

Spherical Harmonic Spinors $\Omega_{j\ell m}$

$$\Omega_{j\ell m} = \begin{pmatrix} Y_{\ell\left(m_{\ell'}=m-\frac{1}{2}\right)}(\hat{r})\left\langle \ell,\left(m_{\ell'}=m-\frac{1}{2}\right),\frac{1}{2},\frac{1}{2}\middle|\left(\ell\frac{1}{2}\right)jm\right\rangle \\ Y_{\ell\left(m_{\ell'}=m+\frac{1}{2}\right)}(\hat{r})\left\langle \ell,\left(m_{\ell'}=m+\frac{1}{2}\right),\frac{1}{2},-\frac{1}{2}\middle|\left(\ell\frac{1}{2}\right)jm\right\rangle \end{pmatrix}_{2\text{ rows}\times 1\text{ column}}$$

for $j=\ell+\frac{1}{2}$

$$\Omega_{j\ell m} = \begin{pmatrix} \sqrt{\frac{j+m}{2j}}\,Y_{\left(\ell=j-\frac{1}{2}\right),\left(m_{\ell'}=m-\frac{1}{2}\right)}(\hat{r}) \\ \sqrt{\frac{j-m}{2j}}\,Y_{\left(\ell=j-\frac{1}{2}\right),\left(m_{\ell'}=m+\frac{1}{2}\right)}(\hat{r}) \end{pmatrix}$$

for $j=\ell-\frac{1}{2}$

$$\Omega_{j\ell m} = \begin{pmatrix} -\sqrt{\frac{j-m+1}{2j+2}}\,Y_{\left(\ell=j+\frac{1}{2}\right),\left(m_{\ell'}=m-\frac{1}{2}\right)}(\hat{r}) \\ \sqrt{\frac{j+m+1}{2j+2}}\,Y_{\left(\ell=j+\frac{1}{2}\right),\left(m_{\ell'}=m+\frac{1}{2}\right)}(\hat{r}) \end{pmatrix}$$

http://nptel.iitm.ac.in/courses/115106057/14
to
http://nptel.iitm.ac.in/courses/115106057/19

$$Z = 12$$

Slater determinant

$$\psi_1^{SD} = 1s_{\frac{1}{2}}^2 2s_{\frac{1}{2}}^2 2p_{\frac{1}{2}}^2 2p_{\frac{3}{2}}^4 3s_{\frac{1}{2}}^2$$

$$\psi_2^{SD} = 1s_{\frac{1}{2}}^2 2s_{\frac{1}{2}}^2 2p_{\frac{1}{2}}^2 2p_{\frac{3}{2}}^4 3p_{\frac{1}{2}}^2$$

….. Many different Slater determinants can be used!

Multi-configuration Hartree-Fock:

CI: Configuration Interaction

Many-Body Correlations

$$Z = \textcircled{12} \quad Mg: 1s^2 2s^2 2p^6 3s^2$$

$$1s^2_{\frac{1}{2}} 2s^2_{\frac{1}{2}} 2p^2_{\frac{1}{2}} 2p^4_{\frac{3}{2}} 3s^2_{\frac{1}{2}} \qquad |\alpha\rangle = \left| n_\alpha l_\alpha j_\alpha m_{j_\alpha} \right\rangle$$

1s½ 3s½ $\ell = 0$

$$\begin{bmatrix} u_{n=1,l=0,j=\frac{1}{2},m_j=\frac{1}{2}}(q_1) & \ldots\ldots\ldots & u_{n=1,l=0,j=\frac{1}{2},m_j=\frac{1}{2}}(q_{12}) \\ \ldots\ldots\ldots & \ldots\ldots\ldots & \ldots\ldots\ldots \\ \ldots\ldots\ldots & \ldots\ldots\ldots & \ldots\ldots\ldots \\ u_{n=3,l=0,j=\frac{1}{2},m_j=-\frac{1}{2}}(q_1) & \ldots\ldots\ldots & u_{n=3,l=0,j=\frac{1}{2},m_j=-\frac{1}{2}}(q_{12}) \end{bmatrix}$$

$$Z = 12$$

Slater determinant

$$\psi_1^{SD} = 1s_{\frac{1}{2}}^2\, 2s_{\frac{1}{2}}^2\, 2p_{\frac{1}{2}}^2\, 2p_{\frac{3}{2}}^4\, 3s_{\frac{1}{2}}^2$$

$$\psi_2^{SD} = 1s_{\frac{1}{2}}^2\, 2s_{\frac{1}{2}}^2\, 2p_{\frac{1}{2}}^2\, 2p_{\frac{3}{2}}^4\, 3p_{\frac{1}{2}}^2$$

$$\begin{bmatrix} u_{n=1,l=0,j=\frac{1}{2},m_j=\frac{1}{2}}(q_1) & \cdots\cdots\cdots & u_{n=1,l=0,j=\frac{1}{2},m_j=\frac{1}{2}}(q_{12}) \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\ \cdots\cdots\cdots & \cdots\cdots\cdots & \cdots\cdots\cdots \\ u_{n=3,l=1,j=\frac{1}{2},m_j=-\frac{1}{2}}(q_1) & \cdots\cdots\cdots & u_{n=3,l=1,j=\frac{1}{2},m_j=-\frac{1}{2}}(q_{12}) \end{bmatrix}$$

$1s_{½}$

$3p_{½}$

$\ell = 1$

$Z = 12$

Slater determinant

$$\psi_1^{SD} = 1s_{\frac{1}{2}}^2\, 2s_{\frac{1}{2}}^2\, 2p_{\frac{1}{2}}^2\, 2p_{\frac{3}{2}}^4\, 3s_{\frac{1}{2}}^2$$

$$\psi_2^{SD} = 1s_{\frac{1}{2}}^2\, 2s_{\frac{1}{2}}^2\, 2p_{\frac{1}{2}}^2\, 2p_{\frac{3}{2}}^4\, 3p_{\frac{1}{2}}^2$$

$$\psi_{Z=12}^{\text{configuration interaction}} = \sum_{i=1}^{n} c_i \psi_i^{SD}$$

Each determinant would have *12!* terms…..

Compact way of handling this situation:

Occupation number formalism

2nd quantization

$q, p \rightarrow q_{op}, p_{op}$: First quantization

$\psi \rightarrow \psi_{op}$: Second (field) quantization

$$Z = 12$$

Slater determinant

$$\psi_1^{SD} = 1s_{\frac{1}{2}}^2 2s_{\frac{1}{2}}^2 2p_{\frac{1}{2}}^2 2p_{\frac{3}{2}}^4 3s_{\frac{1}{2}}^2$$

$$\psi_2^{SD} = 1s_{\frac{1}{2}}^2 2s_{\frac{1}{2}}^2 2p_{\frac{1}{2}}^2 2p_{\frac{3}{2}}^4 3p_{\frac{1}{2}}^2$$

Compact way of handling this situation:

Occupation number formalism

2nd quantization

$$\psi_{Z=12}^{\substack{\text{configuration}\\\text{interaction}}} = \sum_{i=1}^{n} c_i \psi_i^{SD}$$

Slater determinant ⇌ particular configuration

creation & destruction operators

defined by occupation numbers

$$\psi_1^{SD} = 1s_{\frac{1}{2}}^2\, 2s_{\frac{1}{2}}^2\, 2p_{\frac{1}{2}}^2\, 2p_{\frac{3}{2}}^4\, 3s_{\frac{1}{2}}^2$$

1s

1] $\left(n=1, l=0, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,

2] $\left(n=1, l=0, j=\frac{1}{2}, m_j=-\frac{1}{2}\right)$,

2s

3] $\left(n=2, l=0, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,

4] $\left(n=2, l=0, j=\frac{1}{2}, m_j=-\frac{1}{2}\right)$,

2p½

5] $\left(n=2, l=1, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,

6] $\left(n=2, l=1, j=\frac{1}{2}, m_j=\frac{-1}{2}\right)$,

2p3/2

7] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{3}{2}\right)$,

8] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{1}{2}\right)$,

9] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{-1}{2}\right)$,

10] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{-3}{2}\right)$

3s

11] $\left(n=3, l=0, j=\frac{1}{2}, m_j=\frac{1}{2}\right)$,

12] $\left(n=3, l=0, j=\frac{1}{2}, m_j=-\frac{1}{2}\right)$

$$\psi_1^{SD} = 1s_{\frac{1}{2}}^2 2s_{\frac{1}{2}}^2 2p_{\frac{1}{2}}^2 2p_{\frac{3}{2}}^4 3p_{\frac{1}{2}}^2$$

1s

1] $\left(n=1, l=0, j=\frac{1}{2}, m_j=\frac{1}{2}\right),$

2] $\left(n=1, l=0, j=\frac{1}{2}, m_j=-\frac{1}{2}\right),$

2s

3] $\left(n=2, l=0, j=\frac{1}{2}, m_j=\frac{1}{2}\right),$

4] $\left(n=2, l=0, j=\frac{1}{2}, m_j=-\frac{1}{2}\right),$

$2p^{1/2}$

5] $\left(n=2, l=1, j=\frac{1}{2}, m_j=\frac{1}{2}\right),$

6] $\left(n=2, l=1, j=\frac{1}{2}, m_j=\frac{-1}{2}\right),$

$2p^{3/2}$

7] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{3}{2}\right),$

8] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{1}{2}\right),$

9] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{-1}{2}\right),$

10] $\left(n=2, l=1, j=\frac{3}{2}, m_j=\frac{-3}{2}\right)$

3p

13] $\left(n=3, l=1, j=\frac{1}{2}, m_j=\frac{1}{2}\right),$

14] $\left(n=3, l=1, j=\frac{1}{2}, m_j=-\frac{1}{2}\right)$

Description of N-particle system

C.S.C.O. → complete set 'α' of compatible observables

→ complete set 'α' of dynamical variables

→Appropriate for each individual particle

Our system: N number of identical elementary particles

eg. a particular state of our N-particles system:

n_1 particles are in state α_1

n_2 particles are in state α_2

n_3 particles are in state α_3 … etc.

More general states: Linear superposition of such states

….even in the presence of "correlations"

indistinguishable 'elementary particles'

C.S.C.O. → complete set ‘α’ of compatible observables

Our system: N number of identical elementary particles

….even in the presence of “correlations”
indistinguishable ‘elementary particles’

eg. a particular state of our N-particles system:

n_1 particles are in state α_1

n_2 particles are in state α_2

n_3 particles are in state α_3 … etc.

N_1, N_2, N_3 ***Complete set of commuting Hermitian operators***

Eigenvalues respectively of occupation number operators

Description of : Bose-Einstein & Fermi-Dirac particles

State Vector Space / Occupation Number Space

Fock Space

$$\left| n_1, \;\; n_2, \;\; n_3, ... \right\rangle$$ ←← Complete set of orthonormal basis vectors for the many-particle system (identical particals)

$$\updownarrow \;\; \updownarrow \;\; \updownarrow$$

$$\left\{ \alpha_1, \alpha_2, \alpha_3, ... \right\}$$

Arranged in some pre-determined sequence.

C.S.C.O. → complete set 'α' of compatible observables

$$\psi^{(0)}_{vacuum} = \left| 0,0,0,.....0,0,.... \right\rangle$$

One-particle (*in the i^th^*) state

$$\psi^{(1)}_{i} = \left| 0,0,...n_{j \neq i} = 0..,n_i = 1,0,.. \right\rangle$$

Primary References for HF SCF method

- Intermediate quantum mechanics
  Hans A. Bethe and Roman W. Jackiw (Addison-Wesley, 1997)
- Physics of atoms and molecules
  B. H. Bransden and C. J. Joachain (Prentice Hall, 2003)
- P. C. Deshmukh, Alak Banik and Dilip Angom
  Hartree-Fock Self-Consistent Field Method for Many-Electron Systems

Invited article in DST-SERC-School publication (Narosa, November 2011); collection of articles based on lecture course given at the DST-SERC School at the Birla Institute of Technology, Pilani, January 9-28, 2011.
http://www.physics.iitm.ac.in/~labs/amp/homepage/DST_SERC_School_Publications/PCD-100-SCF.pdf

Video Lectures: http://nptel.iitm.ac.in/courses/115106057/20 to …./24

Primary References for 2nd Quantization and Occupation Number formalism…

- A.L.Fetter and J.D.Walecka - Quantum Theory of Many-particle Systems (McGraw Hill, 1971)

Questions? Write to: pcd@physics.iitm.ac.in

- S.Raimes Many Electron Theory (North-Holland, 1972)

Select/Special Topics from
‘Theory of Atomic Collisions and Spectroscopy’

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Unit 2 Lecture Number 14

Second Quantization
Creation, Destruction and Number operators

C.S.C.O. → complete set 'α' of compatible observables

Our system: N number of identical elementary particles

….even in the presence of "correlations"
indistinguishable 'elementary particles'

eg. a particular state of our N-particles system:

n_1 particles are in state α_1

n_2 particles are in state α_2

n_3 particles are in state α_3 … etc.

N_1 N_2 N_3 ***Complete set of commuting Hermitian operators***

Eigenvalues respectively of occupation number operators

Description of : Bose-Einstein & Fermi-Dirac particles

Reference: Fetter & Walecka - 'Quantum Theory of Many Particle Systems' Chapter 1

In almost all cases of interest, the many-particle Hamiltonian has the following form: (for *both* Fermions/Bosons)

$$H = \sum_{k=1}^{N} T(x_k) + \frac{1}{2} \sum_{k=1}^{N} \sum_{\substack{l=1 \\ k \neq l}}^{N} V(x_k, x_l)$$

$eg.\ \ x_k \to space-spin$ $coordinate\ of\ fermions$

$$i\hbar \frac{\partial}{\partial t} \Psi(x_1, x_2, ..., x_N, t) = H\Psi(x_1, x_2, ..., x_N, t)$$

Schrodinger equation

-with appropriate boundary conditions on the wave function

Ψ : expressed in basis of single particle base functions $\psi_{E_k}(x_k)$

$eg.:\quad \psi_{E_k}(x_k) \leftrightarrow \psi_{n_k l_k m_{l_k} m_{s_k}}(x_k)$ or $\psi_{E_k}(x_k) \leftrightarrow \psi_{n_k l_k j_k m_{j_k}}(x_k)$

$E_k \leftrightarrow \{n_k l_k m_{l_k} m_{s_k}\}$ or $E_k \leftrightarrow \{n_k l_k j_k m_{j_k}\}$

eigenvalues of 'one-electron' C.S.C.O.

$$i\hbar \frac{\partial}{\partial t}\Psi\left(x_1,x_2,...,x_N,t\right)=H\Psi\left(x_1,x_2,...,x_N,t\right)$$

(for *both* Fermions/Bosons)

$$\Psi\left(x_1,x_2,..,x_N,t\right)=\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'} C\left(E_1',E_2',..,E_N',t\right)\psi_{E_1'}\left(x_1\right)\psi_{E_2'}\left(x_2\right)..\psi_{E_N'}\left(x_N\right)$$

$$\Psi\left(x_1,x_2,..,x_N,t\right)=\sum_{E_1',E_2',..,E_N'} C\left(E_1',E_2',..,E_N',t\right)\psi_{E_1'}\left(x_1\right)\psi_{E_2'}\left(x_2\right)..\psi_{E_N'}\left(x_N\right)$$

$\psi_{E_k}\left(x_k\right)$: time-<u>independent</u> one-particle functions

$eg.:\ \psi_{E_k}\left(x_k\right)\leftrightarrow\psi_{n_k l_k m_{l_k} m_{s_k}}\left(x_k\right)$ or $\psi_{E_k}\left(x_k\right)\leftrightarrow\psi_{n_k l_k j_k m_{j_k}}\left(x_k\right)$

entire time–dependence of $\Psi\left(x_1,x_2,..,x_N,t\right)$
is in the time–dependence of $C\left(E_1',E_2',..,E_N',t\right)$

$$i\hbar\frac{\partial}{\partial t}\Psi\left(x_1,x_2,...,x_N,t\right)=H\Psi\left(x_1,x_2,...,x_N,t\right)$$

(for *both* Fermions/Bosons)

$$\Psi\left(x_1,x_2,..,x_N,t\right)=\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C\left(E_1',E_2',..,E_N',t\right)\psi_{E_1'}\left(x_1\right)\psi_{E_2'}\left(x_2\right)..\psi_{E_N'}\left(x_N\right)$$

$$i\rightleftharpoons j$$

$$\Psi\left(x_1,x_2,..,x_i,...x_j,....x_N,t\right)=\pm\Psi\left(x_1,x_2,..,x_j,...x_i,....x_N,t\right)$$

$+\ Bosons$ ⇐ ⇒ $-\ Fermions$

Necessary and sufficient condition is that the expansion coefficients themselves are symmetric or antisymmetric with respect to interchange corresponding quantum numbers.

$+B$ ⇐ ⇒ $-F$

$$C\left(E_1,E_2,..,E_i,..,E_j,..E_N,t\right)=\pm C\left(E_1,E_2,..,E_j,..,E_i,..E_N,t\right)$$

HW: *prove it!* $i\rightleftharpoons j$

$$i\hbar\frac{\partial}{\partial t}\Psi(x_1,x_2,...,x_N,t)=H\Psi(x_1,x_2,...,x_N,t)$$ (for *both* Fermions/Bosons)

$$\Psi(x_1,x_2,..,x_N,t)=\sum_{E_1',E_2',..,E_N'}C(E_1',E_2',..,E_N',t)\psi_{E_1'}(x_1)\psi_{E_2'}(x_2)..\psi_{E_N'}(x_N)$$

$$\Psi(x_1,x_2,..,x_N,t)=\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C(E_1',E_2',..,E_N',t)\psi_{E_1'}(x_1)\psi_{E_2'}(x_2)..\psi_{E_N'}(x_N)$$

multiply the Schrodinger equation by $\psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger$

for a fixed set $\{E_1,E_2,..E_N\}$

$$\psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times i\hbar\frac{\partial}{\partial t}\Psi(x_1,x_2,...,x_N,t)=$$

$$=\psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times H\Psi(x_1,x_2,...,x_N,t)$$

Now, integrate over all coordinates

$$i\hbar\int dx_1\int dx_2..\int dx_N\ \ \psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times\frac{\partial}{\partial t}\Psi(x_1,x_2,...,x_N,t)=$$

$$=\int dx_1\int dx_2..\int dx_N\ \ \psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times H\Psi(x_1,x_2,...,x_N,t)$$

$$i\hbar\int dx_1\int dx_2..\int dx_N\ \ \psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times\frac{\partial}{\partial t}\Psi(x_1,x_2,...,x_N,t)=$$

$$=\int dx_1\int dx_2..\int dx_N\ \ \psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times H\Psi(x_1,x_2,...,x_N,t)$$

$$\Psi(x_1,x_2,..,x_N,t)=\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C(E_1',E_2',..,E_N',t)\psi_{E_1'}(x_1)\psi_{E_2'}(x_2)..\psi_{E_N'}(x_N)$$

$$i\hbar\int dx_1\int dx_2..\int dx_N\left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times\\ \frac{\partial}{\partial t}\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C(E_1',E_2',..,E_N',t)\psi_{E_1'}(x_1)\psi_{E_2'}(x_2)..\psi_{E_N'}(x_N)\end{array}\right]=$$

$$=\int dx_1\int dx_2..\int dx_N\left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times\\ H\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C(E_1',E_2',..,E_N',t)\psi_{E_1'}(x_1)\psi_{E_2'}(x_2)..\psi_{E_N'}(x_N)\end{array}\right]$$

$$i\hbar \int dx_1 \int dx_2 .. \int dx_N \left[\begin{array}{l} \psi_{E_1}(x_1)^\dagger \psi_{E_2}(x_2)^\dagger .. \psi_{E_N}(x_N)^\dagger \times \\ \frac{\partial}{\partial t} \sum_{E_1'} \sum_{E_2'} .. \sum_{E_N'} C(E_1', E_2', .., E_N', t) \psi_{E_1'}(x_1) \psi_{E_2'}(x_2) .. \psi_{E_N'}(x_N) \end{array} \right] =$$

$$= \int dx_1 \int dx_2 .. \int dx_N \left[\begin{array}{l} \psi_{E_1}(x_1)^\dagger \psi_{E_2}(x_2)^\dagger .. \psi_{E_N}(x_N)^\dagger \times \\ H \sum_{E_1'} \sum_{E_2'} .. \sum_{E_N'} C(E_1', E_2', .., E_N', t) \psi_{E_1'}(x_1) \psi_{E_2'}(x_2) .. \psi_{E_N'}(x_N) \end{array} \right]$$

$$\int dx_k \; \psi_{E_i}(x_k)^\dagger \psi_{E_i'}(x_k) = \delta_{E_i E_i'}$$

$$i\hbar \frac{\partial}{\partial t} C(E_1, E_2, .., E_N, t) =$$

$$= \int dx_1 \int dx_2 .. \int dx_N \left[\begin{array}{l} \psi_{E_1}(x_1)^\dagger \psi_{E_2}(x_2)^\dagger .. \psi_{E_N}(x_N)^\dagger \times \\ H \sum_{E_1'} \sum_{E_2'} .. \sum_{E_N'} C(E_1', E_2', .., E_N', t) \psi_{E_1'}(x_1) \psi_{E_2'}(x_2) .. \psi_{E_N'}(x_N) \end{array} \right]$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right)=$$

$$=\int dx_1\int dx_2..\int dx_N\left[\begin{array}{l}\psi_{E_1}\left(x_1\right)^\dagger\psi_{E_2}\left(x_2\right)^\dagger..\psi_{E_N}\left(x_N\right)^\dagger\times\\ H\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C\left(E_1',E_2',..,E_N',t\right)\psi_{E_1'}\left(x_1\right)\psi_{E_2'}\left(x_2\right)..\psi_{E_N'}\left(x_N\right)\end{array}\right]$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right)=$$

$$=\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C\left(E_1',E_2',..,E_N',t\right)\int dx_1\int dx_2..\int dx_N\left[\begin{array}{l}\psi_{E_1}\left(x_1\right)^\dagger\psi_{E_2}\left(x_2\right)^\dagger..\psi_{E_N}\left(x_N\right)^\dagger\times\\ H\psi_{E_1'}\left(x_1\right)\psi_{E_2'}\left(x_2\right)..\psi_{E_N'}\left(x_N\right)\end{array}\right]$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right)=$$

$$=\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C\left(E_1',E_2',..,E_N',t\right)\int dx_1\int dx_2..\int dx_N\left[\begin{array}{l}\psi_{E_1}\left(x_1\right)^\dagger\psi_{E_2}\left(x_2\right)^\dagger..\psi_{E_N}\left(x_N\right)^\dagger\times\\ \left\{\sum_{k=1}^{N}T(x_k)+\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1\\ \boxed{k\neq l}}}^{N}V(x_k,x_l)\right\}\psi_{E_1'}\left(x_1\right)\psi_{E_2'}\left(x_2\right)..\psi_{E_N'}\left(x_N\right)\end{array}\right]$$

$$H=\left\{\sum_{k=1}^{N}T(x_k)+\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1\\ \boxed{k\neq l}}}^{N}V(x_k,x_l)\right\}$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right)=$$

$$=\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C\left(E_1',E_2',..,E_N',t\right)\int dx_1\int dx_2..\int dx_N\left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times\\ \left\{\sum_{k=1}^{N}T(x_k)+\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1\\ k\neq l}}^{N}V(x_k,x_l)\right\}\psi_{E_1'}(x_1)\psi_{E_2'}(x_2)..\psi_{E_N'}(x_N)\end{array}\right]$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right)=$$

$$=\left[\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C\left(E_1',..,E_N',t\right)\int dx_1..\int dx_N\left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger..\psi_{E_N}(x_N)^\dagger\times\\ \left\{\sum_{k=1}^{N}T(x_k)\right\}\psi_{E_1'}(x_1)..\psi_{E_N'}(x_N)\end{array}\right]+\right.$$

$$\left.+\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C\left(E_1',..,E_N',t\right)\int dx_1..\int dx_N\left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger..\psi_{E_N}(x_N)^\dagger\times\\ \left\{\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1\\ k\neq l}}^{N}V(x_k,x_l)\right\}\psi_{E_1'}(x_1)..\psi_{E_N'}(x_N)\end{array}\right]\right]$$

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) =$$

$$= \Bigg[\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'} C(E_1',..,E_N',t)\int dx_1..\int dx_N \left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger..\psi_{E_N}(x_N)^\dagger\times \\ \left\{\sum_{k=1}^{N}T(x_k)\right\}\psi_{E_1'}(x_1)..\psi_{E_N'}(x_N)\end{array}\right] +$$

$$+\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'} C(E_1',..,E_N',t)\int dx_1..\int dx_N \left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger..\psi_{E_N}(x_N)^\dagger\times \\ \left\{\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1 \\ k\neq l}}^{N} V(x_k,x_l)\right\}\psi_{E_1'}(x_1)..\psi_{E_N'}(x_N)\end{array}\right]\Bigg]$$

Integration of the one-particle terms over independent degrees of freedom

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) = \sum_{E_1'}..\sum_{E_N'}\sum_{k=1}^{N}\left\{\begin{array}{l}C(E_1',..,E_N',t)\times \\ \int dx_k\psi_{E_k}(x_k)^\dagger\{T(x_k)\}\psi_{E_k'}(x_k)\int dx_1\psi_{E_1}(x_1)^\dagger\psi_{E_1'}(x_1)..\int dx_N\psi_{E_N}(x_N)^\dagger\psi_{E_N'}(x_N)\end{array}\right\} +$$

$$+\sum_{E_1'}..\sum_{E_N'} C(E_1',..,E_N',t)\int dx_1..\int dx_N \left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger..\psi_{E_N}(x_N)^\dagger\times \\ \left\{\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1 \\ k\neq l}}^{N} V(x_k,x_l)\right\}\psi_{E_1'}(x_1)..\psi_{E_N'}(x_N)\end{array}\right]$$

$$i\hbar \frac{\partial}{\partial t} C(E_1, E_2, .., E_N, t) =$$

$$= \sum_{E_1'} .. \sum_{E_N'} \sum_{k=1}^{N} \left\{ \begin{array}{l} C(E_1', .., E_N', t) \times \\ \times \int dx_k \psi_{E_k}(x_k)^\dagger \{T(x_k)\} \psi_{E_k'}(x_k) \times \\ \\ \times \int dx_1 \psi_{E_1}(x_1)^\dagger \psi_{E_1'}(x_1) .. \times \\ \\ \times \int dx_N \psi_{E_N}(x_N)^\dagger \psi_{E_N'}(x_N) \end{array} \right\} +$$

Orthogonality and summation over E_1' etc.

$$+ \sum_{E_1'} .. \sum_{E_N'} C(E_1', .., E_N', t) \int dx_1 .. \int dx_N \left[\begin{array}{l} \psi_{E_1}(x_1)^\dagger .. \psi_{E_N}(x_N)^\dagger \times \\ \left\{ \frac{1}{2} \sum_{k=1}^{N} \sum_{\substack{l=1 \\ k \neq l}}^{N} V(x_k, x_l) \right\} \psi_{E_1'}(x_1) .. \psi_{E_N'}(x_N) \end{array} \right]$$

$$i\hbar \frac{\partial}{\partial t} C(E_1, E_2, .., E_N, t) =$$

$$= \sum_{E_1'} .. \sum_{E_N'} \sum_{k=1}^{N} C(E_1', .., E_N', t) \int dx_k \psi_{E_k}(x_k)^\dagger \{T(x_k)\} \psi_{E_k'}(x_k) \int dx_1 \psi_{E_1}(x_1)^\dagger \psi_{E_1'}(x_1) .. \int dx_N \psi_{E_N}(x_N)^\dagger \psi_{E_N'}(x_N) +$$

$$+ \sum_{E_1'} .. \sum_{E_N'} C(E_1', .., E_N', t) \int dx_1 .. \int dx_N \begin{bmatrix} \psi_{E_1}(x_1)^\dagger .. \psi_{E_N}(x_N)^\dagger \times \\ \left\{ \frac{1}{2} \sum_{k=1}^{N} \sum_{\substack{l=1 \\ k \neq l}}^{N} V(x_k, x_l) \right\} \psi_{E_1'}(x_1) .. \psi_{E_N'}(x_N) \end{bmatrix}$$

Orthogonality and summation over E_1' etc.

$$i\hbar \frac{\partial}{\partial t} C(E_1, E_2, .., E_N, t) = \sum_{E_k'} \sum_{k=1}^{N} C(E_1, .., E_k', .., E_N, t) \int dx_k \psi_{E_k}(x_k)^\dagger T(x_k) \psi_{E_k'}(x_k) +$$

$$+ \sum_{E_1'} .. \sum_{E_N'} C(E_1', .., E_N', t) \int dx_1 .. \int dx_N \begin{bmatrix} \psi_{E_1}(x_1)^\dagger .. \psi_{E_N}(x_N)^\dagger \times \\ \left\{ \frac{1}{2} \sum_{k=1}^{N} \sum_{\substack{l=1 \\ k \neq l}}^{N} V(x_k, x_l) \right\} \psi_{E_1'}(x_1) .. \psi_{E_N'}(x_N) \end{bmatrix}$$

$$
i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) = \sum_{E_k'}\sum_{k=1}^{N} C(E_1,..,E_k',..,E_N,t)\int dx_k \psi_{E_k}(x_k)^\dagger T(x_k)\psi_{E_k'}(x_k) +
$$

$$
+\sum_{E_1'}..\sum_{E_N'} C(E_1',..,E_N',t)\int dx_1..\int dx_N \left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger..\psi_{E_N}(x_N)^\dagger \times \\ \left\{\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1 \\ k\neq l}}^{N} V(x_k,x_l)\right\}\psi_{E_1'}(x_1)..\psi_{E_N'}(x_N)\end{array}\right]
$$

writing W instead of E_k'

$$
i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) = \sum_{W}\sum_{k=1}^{N} C(E_1,..,E_{k-1},W,E_{k+1},..E_N,t)\int dx_k \psi_{E_k}(x_k)^\dagger T(x_k)\psi_W(x_k) +
$$

$$
+\sum_{E_1'}..\sum_{E_N'} C(E_1',..,E_N',t)\int dx_1..\int dx_N \left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger..\psi_{E_N}(x_N)^\dagger \times \\ \left\{\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1 \\ k\neq l}}^{N} V(x_k,x_l)\right\}\psi_{E_1'}(x_1)..\psi_{E_N'}(x_N)\end{array}\right]
$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right) = \sum_W \sum_{k=1}^{N} C\left(E_1,..,E_{k-1},W,E_{k+1},..E_N,t\right)\int dx_k \psi_{E_k}\left(x_k\right)^\dagger T(x_k)\psi_W\left(x_k\right)+$$

$$+\sum_{E_1'}..\sum_{E_N'} C\left(E_1',..,E_N',t\right)\int dx_1..\int dx_N \left[\begin{array}{l}\psi_{E_1}\left(x_1\right)^\dagger..\psi_{E_N}\left(x_N\right)^\dagger\times \\ \left\{\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1 \\ k\neq l}}^{N} V(x_k,x_l)\right\}\psi_{E_1'}\left(x_1\right)..\psi_{E_N'}\left(x_N\right)\end{array}\right]$$

Now, focus on the 2 – ***particles*** term:

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right) =$$

$$=\sum_W \sum_{k=1}^{N} C\left(E_1,..,E_{k-1},W,E_{k+1},..E_N,t\right)\int dx_k \psi_{E_k}\left(x_k\right)^\dagger T(x_k)\psi_W\left(x_k\right)+$$

$$+\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1 \\ k\neq l}}^{N}\sum_{E_1'}..\sum_{E_N'}\left\{\begin{array}{l}C\left(E_1',..,E_N',t\right)\times \\ \times\int dx_1..\int dx_N \left[\psi_{E_1}\left(x_1\right)^\dagger..\psi_{E_N}\left(x_N\right)^\dagger V(x_k,x_l)\psi_{E_1'}\left(x_1\right)..\psi_{E_N'}\left(x_N\right)\right]\end{array}\right\}$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right) \quad =$$

$$=\sum_W\sum_{k=1}^{N}C\left(E_1,..,E_{k-1},W,E_{k+1},..E_N,t\right)\int dx_k\psi_{E_k}\left(x_k\right)^{\dagger}T(x_k)\psi_W\left(x_k\right)+$$

$$+\frac{1}{2}\sum_{\substack{k=1\\ \boxed{k\neq l}}}^{N}\sum_{l=1}^{N}\sum_{E_1'}..\sum_{E_N'}\left\{\begin{matrix}C\left(E_1',..,E_N',t\right)\times\\ \times\int dx_1..\int dx_N\ \left[\psi_{E_1}\left(x_1\right)^{\dagger}..\psi_{E_N}\left(x_N\right)^{\dagger}V(x_k,x_l)\psi_{E_1'}\left(x_1\right)..\psi_{E_N'}\left(x_N\right)\right]\end{matrix}\right\}$$

Due to orthogonality of single particle wavefunctions integrations over all coordinates except x_k *and* x_l give Kronecker deltas….

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right) \ = \sum_W\sum_{k=1}^{N}C\left(E_1,..,E_{k-1},W,E_{k+1},..E_N,t\right)\int dx_k\psi_{E_k}\left(x_k\right)^{\dagger}T(x_k)\psi_W\left(x_k\right)+$$

$$+\frac{1}{2}\sum_{\substack{k=1\\ \boxed{k\neq l}}}^{N}\sum_{l=1}^{N}\sum_{E_1'}..\sum_{E_N'}C\left(E_1',..,E_N',t\right)\underbrace{\int dx_k\int dx_l\psi_{E_k}\left(x_k\right)^{\dagger}\psi_{E_l}\left(x_l\right)^{\dagger}V(x_k,x_l)\psi_{E_k'}\left(x_k\right)\psi_{E_l'}\left(x_l\right)}\underbrace{\delta_{E_1'E_1}..\delta_{E_N'E_N}}$$

integrations over x_k *and* x_l

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) = \sum_W \sum_{k=1}^{N} C(E_1,..,E_{k-1},W,E_{k+1},..E_N,t)\int dx_k \psi_{E_k}(x_k)^\dagger T(x_k)\psi_W(x_k) +$$

$$+\frac{1}{2}\sum_{\substack{k=1\\k\neq l}}^{N}\sum_{l=1}^{N}\sum_{E_1'}..\sum_{E_N'} C(E_1',..,E_N',t)\int dx_k\int dx_l \psi_{E_k}(x_k)^\dagger \psi_{E_l}(x_l)^\dagger V(x_k,x_l)\psi_{E_k'}(x_k)\psi_{E_l'}(x_l)\delta_{E_1'E_1}..\delta_{E_N'E_N}$$

summing over E_1', and E_2' etc. & exploiting $\delta_{E_1'E_1}$ etc.

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) = \sum_W \sum_{k=1}^{N} \left\{ \begin{array}{l} C(E_1,..,E_{k-1},W,E_{k+1},..E_N,t)\times \\ \times\int dx_k \psi_{E_k}(x_k)^\dagger T(x_k)\psi_W(x_k) \end{array} \right\} +$$

$$+\frac{1}{2}\sum_{\substack{k=1\\k\neq l}}^{N}\sum_{l=1}^{N}\sum_{E_k'}\sum_{E_l'} \left\{ \begin{array}{l} C(E_1,..E_k',..,E_l',..E_N,t)\times \\ \times\int dx_k\int dx_l \psi_{E_k}(x_k)^\dagger \psi_{E_l}(x_l)^\dagger V(x_k,x_l)\psi_{E_k'}(x_k)\psi_{E_l'}(x_l) \end{array} \right\}$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right) = \sum_{W}\sum_{k=1}^{N}\begin{Bmatrix} C\left(E_1,..,E_{k-1},W,E_{k+1},..E_N,t\right)\times \\ \times\int dx_k \psi_{E_k}\left(x_k\right)^{\dagger} T(x_k)\psi_W\left(x_k\right) \end{Bmatrix}+$$

$$+\frac{1}{2}\sum_{\substack{k=1 \\ k\neq l}}^{N}\sum_{l=1}^{N}\sum_{E_k'}\sum_{E_l'}\begin{Bmatrix} C\left(E_1,..E_k',..,E_l',..E_N,t\right)\times \\ \times\int dx_k\int dx_l \psi_{E_k}\left(x_k\right)^{\dagger}\psi_{E_l}\left(x_l\right)^{\dagger} V(x_k,x_l)\psi_{E_k'}\left(x_k\right)\psi_{E_l'}\left(x_l\right) \end{Bmatrix}$$

writing W instead of E_k', and W' instead of E_l'

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right) = \sum_{W}\sum_{k=1}^{N}\begin{Bmatrix} C\left(E_1,..,E_{k-1},W,E_{k+1},..E_N,t\right)\times \\ \times\int dx_k \psi_{E_k}\left(x_k\right)^{\dagger} T(x_k)\psi_W\left(x_k\right) \end{Bmatrix}+$$

$$+\frac{1}{2}\sum_{\substack{k=1 \\ k\neq l}}^{N}\sum_{l=1}^{N}\sum_{W}\sum_{W'}\begin{Bmatrix} C\left(E_1,..,E_{k-1},W,E_{k+1},..,E_{l-1},W',E_{l+1},..E_N,t\right)\times \\ \times\int dx_k\int dx_l \psi_{E_k}\left(x_k\right)^{\dagger}\psi_{E_l}\left(x_l\right)^{\dagger} V(x_k,x_l)\psi_W\left(x_k\right)\psi_{W'}\left(x_l\right) \end{Bmatrix}$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right) = \sum_{W}\sum_{k=1}^{N}\left\{\begin{matrix}C\left(E_1,..,E_{k-1},W,E_{k+1},..E_N,t\right)\times \\ \times\int dx_k\psi_{E_k}\left(x_k\right)^{\dagger}T(x_k)\psi_W\left(x_k\right)\end{matrix}\right\}+$$

$$+\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1 \\ k\neq l}}^{N}\sum_{W}\sum_{W'}\left\{\begin{matrix}C\left(E_1,..,E_{k-1},W,E_{k+1},..,E_{l-1},W',E_{l+1},..E_N,t\right)\times \\ \times\int dx_k\int dx_l\psi_{E_k}\left(x_k\right)^{\dagger}\psi_{E_l}\left(x_l\right)^{\dagger}V(x_k,x_l)\psi_W\left(x_k\right)\psi_{W'}\left(x_l\right)\end{matrix}\right\}$$

statistics :

$$i \rightleftharpoons j$$

$$C\left(E_1,E_2,..,E_i,..,E_j,..E_N,t\right)=\pm C\left(E_1,E_2,..,E_j,..,E_i,..E_N,t\right)$$

$+$ *Bosons* $-$ *Fermions*

Our immediate interest is in: *Electrons* (Fermions)

$$C\left(E_1,E_2,..,E_i,..,E_j,..E_N,t\right)=-C\left(E_1,E_2,..,E_j,..,E_i,..E_N,t\right)$$

$$i \rightleftharpoons j$$

Electrons (Fermions):

$$C\left(E_1, E_2, .., E_i, .., E_j, ..E_N, t\right) = -C\left(E_1, E_2, .., E_j, .., E_i, ..E_N, t\right)$$

If $E_j = E_i$, $C\left(E_1, E_2, .., E_i, .., E_j, ..E_N, t\right) = 0$

Ordered sequence: $E_1, E_2, .., E_i, .., E_j, ..E_N$

Ordering denoted by: $E_1 < E_2 < .. < E_i < .. < E_j < .. < E_N$

Coefficient: $C\left(E_1 < E_2 < .. < E_i < .. < E_j < .. < E_N, t\right)$

all information about which one-electron states are occupied is contained in a coefficient:

$f\left(n_1, n_2, ..n_i, .., n_j, .., ...n_\infty, t\right)$ where $n_i = 0$ or 1

$$f\left(n_1, n_2, ..n_i, .., n_j, .., ...n_\infty, t\right) \equiv C\left(E_1 < E_2 < .. < E_i < .. < E_j < .. < E_N, t\right)$$

$$\equiv \tilde{C}\left(n_1, n_2, ..n_i, .., n_j, .., ...n_\infty, t\right)$$

............FW 1.44

$$i\hbar\frac{\partial}{\partial t}\Psi(x_1,x_2,...,x_N,t)=H\Psi(x_1,x_2,...,x_N,t)$$

$$\Psi(x_1,x_2,...,x_N,t)=\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C(E_1',E_2',...,E_N',t)\psi_{E_1'}(x_1)\psi_{E_2'}(x_2)..\psi_{E_N'}(x_N)$$

$$f(n_1,n_2,..n_i,...,n_j,...,....n_\infty,t)\equiv C(E_1<E_2<..<E_i<..<E_j<..<E_N,t)$$

Many-electron wavefunction:

$$\Psi(x_1,x_2,...,x_N,t)=\sum_{n_1=0}^{1}..\sum_{n_i=0}^{1}..\sum_{n_\infty=0}^{1}f(n_1,n_2,..n_i,..n_\infty,t)\Phi_{n_1,n_2,..n_i,....n_\infty}(x_1,x_2,...x_N)$$

Time-dependence

$$\Phi_{n_1,n_2,..n_i,....n_\infty}(x_1,x_2,...x_N)=\frac{1}{\sqrt{N!}}\begin{vmatrix}\psi_{E_1^0}(x_1) & .. & .. & \psi_{E_1^0}(x_N)\\ .. & & & ..\\ .. & & & ..\\ \psi_{E_N^0}(x_1) & .. & .. & \psi_{E_N^0}(x_N)\end{vmatrix}$$

Slater determinant is time-independent

Occupation number state vector

$$|\Psi(t)\rangle=\sum_{n_1=0}^{1}..\sum_{n_i=0}^{1}..\sum_{n_\infty=0}^{1}f(n_1,..n_i,..n_\infty,t)|n_1,..n_i,....n_\infty\rangle$$

FW 1.47

Fermion occupation number state vector:

$$\left|\Psi(t)\right\rangle = \sum_{n_1=0}^{1} .. \sum_{n_i=0}^{1} .. \sum_{n_\infty=0}^{1} f\left(n_1,..n_i,..n_\infty,t\right)\left|n_1,..n_i,....n_\infty\right\rangle$$

It is operated upon by

Fermion (electron) creation and destruction operators

fundamental anti – commutation rules

for fermion operators:

$$\left[a_r, a_s^\dagger\right]_+ = \delta_{rs} \qquad \left[a_r^\dagger, a_s^\dagger\right]_+ = 0 \qquad \left[a_r, a_s\right]_+ = \delta_{rs}$$

$$anti-commutator \qquad \left[A,B\right]_+ = AB + BA$$

Boson occupation number state vector:

$$|\Psi(t)\rangle = \sum_{n_1} .. \sum_{n_\infty} f(n_1,..n_i,..n_\infty,t)\,|n_1,..n_i,....n_\infty\rangle$$

$$\sum_i n_i = N$$

It is operated upon by
Boson creation and destruction operators

fundamental commutation rules

for boson operators:

$$[b_r, b_s^\dagger]_- = \delta_{rs} \qquad [b_r^\dagger, b_s^\dagger]_- = 0 \qquad [b_r, b_s]_- = 0$$

$$commutator: \qquad [A,B]_- = AB - BA$$

Fermion (electron) creation and destruction operators

Properties

$$|\Psi(t)\rangle = \sum_{n_1=0}^{1} .. \sum_{n_i=0}^{1} .. \sum_{n_\infty=0}^{1} f\left(n_1,..n_i,..n_\infty,t\right)\left|n_1,..n_i,....n_\infty\right\rangle$$

$$fundamental \;\; anti-commutation \; rules$$

for fermion operators:

$$\left[a_r, a_s^{\dagger}\right]_+ = \delta_{rs} \qquad \left[a_r^{\dagger}, a_s^{\dagger}\right]_+ = 0 \qquad \left[a_r, a_s\right]_+ = 0$$

$$a_s^{\dagger} a_s^{\dagger} |0\rangle = ?$$

$$a_s^{\dagger} a_s^{\dagger} = \frac{1}{2} \times 2 a_s^{\dagger} a_s^{\dagger} = \frac{1}{2} \times \left[a_s^{\dagger} a_s^{\dagger} + a_s^{\dagger} a_s^{\dagger}\right]$$

$$= \frac{1}{2} \times \left[a_s^{\dagger}, a_s^{\dagger}\right]_+ = 0$$

Pauli exclusion: you cannot create another fermion in a state occupied already!

Eigenvalue of Fermion 'number' operator: $n_s = a_s^\dagger a_s$

$$fundamental\ \ anti-commutation\ rules\ :$$

$$\left[a_r, a_s^\dagger\right]_+ = \delta_{rs} \qquad \left[a_r^\dagger, a_s^\dagger\right]_+ = 0 \qquad \left[a_r, a_s\right]_+ = 0$$

$$\left[a_s, a_s^\dagger\right]_+ = 1$$

$$n_s = a_s^\dagger a_s = 1 - a_s a_s^\dagger$$

$$\left(a_s^\dagger a_s\right)^2 = \left(1 - a_s a_s^\dagger\right)\left(1 - a_s a_s^\dagger\right)$$

$$= 1 - a_s a_s^\dagger - a_s a_s^\dagger + a_s a_s^\dagger a_s a_s^\dagger$$

$$\left(a_s^\dagger a_s\right)^2 = 1 - a_s a_s^\dagger - a_s a_s^\dagger + a_s\left(1 - a_s a_s^\dagger\right) a_s^\dagger$$

$$= 1 - a_s a_s^\dagger = n_s \qquad \therefore \quad n_s^2 = n_s$$

$$a_s^\dagger a_s^\dagger = 0 \qquad a_s a_s = 0$$

$$i.e.\ \ n_s\left(n_s - 1\right) = 0$$

operator identity

$$eigenvalues\ of\ n_s :\ 0\ \ or\ \ 1$$

$$fundamental\ \ anti-commutation\ rules\ :$$

$$\left[a_r, a_s^\dagger\right]_+ = \delta_{rs} \qquad \left[a_r^\dagger, a_s^\dagger\right]_+ = 0 \qquad \left[a_r, a_s\right]_+ = 0$$

$$n_s = a_s^\dagger a_s \quad \therefore \quad n_s^2 = n_s$$

$a^\dagger a$: Number operator

eigenvalues of n_s : 0 or 1

Number 0 'zero'

$$a^\dagger|1\rangle = 0 \qquad a|0\rangle = 0$$

$a^\dagger$: Creation operator

Vacuum state : $|0\rangle$
No particle

a: Destruction operator

$$a^\dagger|0\rangle = |1\rangle \qquad a|1\rangle = |0\rangle$$

"We might say that the three operators $a^\dagger$, a and $n=a^\dagger a$ correspond respectively to the Creator (Brahma), the Destroyer (Shiva),

and the Preserver (Vishnu) in Hindu mythology"

– J.J.Sakurai in

'Advanced Quantum Mechanics'

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Select/Special Topics from
'Theory of Atomic Collisions and Spectroscopy'

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Unit 2 Lecture Number 15

Many-Particle Hamiltonian & Schrodinger Eq.
in
2^{nd} Quantization formalism

fundamental commutation rules

for boson operators:

commutator: $[A,B]_- = AB - BA$

$$[b_r, b_s^\dagger]_- = \delta_{rs} \qquad [b_r^\dagger, b_s^\dagger]_- = 0 \qquad [b_r, b_s]_- = 0$$

Simple Harmonic Ocscillator (1-D)

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

Hamiltonian in the notation of FIRST QUANTIZATION

Annihilation and Creation operators→

$$b = \left(\sqrt{\frac{m\omega}{2\hbar}}\right)x + i\left(\frac{1}{\sqrt{2\hbar m\omega}}\right)p$$

$$b^\dagger = \left(\sqrt{\frac{m\omega}{2\hbar}}\right)x - i\left(\frac{1}{\sqrt{2\hbar m\omega}}\right)p$$

$$b^\dagger b = \left\{\left(\sqrt{\frac{m\omega}{2\hbar}}\right)x - i\left(\frac{1}{\sqrt{2\hbar m\omega}}\right)p\right\}\left\{\left(\sqrt{\frac{m\omega}{2\hbar}}\right)x + i\left(\frac{1}{\sqrt{2\hbar m\omega}}\right)p\right\}$$

$$b^\dagger b = \left\{ \left(\sqrt{\frac{m\omega}{2\hbar}} \right) x - i \left(\frac{1}{\sqrt{2\hbar m\omega}} \right) p \right\} \left\{ \left(\sqrt{\frac{m\omega}{2\hbar}} \right) x + i \left(\frac{1}{\sqrt{2\hbar m\omega}} \right) p \right\}$$

$$b^\dagger b = \frac{m\omega}{2\hbar} x^2 + \boxed{\frac{i}{2\hbar} xp - \frac{i}{2\hbar} px} + \frac{1}{2\hbar m\omega} p^2$$

$$b^\dagger b = \frac{m\omega}{2\hbar} x^2 + \frac{1}{2\hbar m\omega} p^2 + \frac{i}{2\hbar} [x, p]_-$$

$$b^\dagger b = \frac{m\omega}{2\hbar} x^2 + \frac{1}{2m\hbar\omega} p^2 + \frac{i}{2\hbar} (i\hbar)$$

Simple Harmonic Ocscillator (1-D)

$$H = \frac{1}{2} kx^2 + \frac{p^2}{2m} = \frac{m\omega^2}{2} x^2 + \frac{p^2}{2m}$$

$$b^\dagger b = \frac{1}{\hbar} \left\{ \frac{m\omega}{2} x^2 + \frac{1}{2m\omega} p^2 \right\} - \frac{1}{2}$$

$$\boxed{b^\dagger b = \frac{H}{\hbar\omega} - \frac{1}{2}}$$

SHO Hamiltonian in the notation of

FIRST QUANTIZATION

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2 = \frac{p^2}{2m} + \frac{1}{2}m\omega^2 x^2$$

$$b^\dagger b = \frac{H}{\hbar\omega} - \frac{1}{2}$$

$$H = \left(b^\dagger b + \frac{1}{2} \right)\hbar\omega$$

Hamiltonian in the notation of

SECOND QUANTIZATION

creation and destruction operators

$$H = \left(b^\dagger b + \frac{1}{2} \right) \hbar\omega$$

$$b = \left(\sqrt{\frac{m\omega}{2\hbar}} \right) x + i \left(\frac{1}{\sqrt{2\hbar m\omega}} \right) p$$

$$b^\dagger = \left(\sqrt{\frac{m\omega}{2\hbar}} \right) x - i \left(\frac{1}{\sqrt{2\hbar m\omega}} \right) p$$

$$x = \frac{1}{2} \left(\sqrt{\frac{2\hbar}{m\omega}} \right) (b + b^\dagger) = \left(\sqrt{\frac{\hbar}{2m\omega}} \right) (b + b^\dagger)$$

$$p = \frac{1}{2i} \left(\sqrt{2\hbar m\omega} \right) (b - b^\dagger) = \frac{1}{i} \left(\sqrt{\frac{\hbar m\omega}{2}} \right) (b - b^\dagger)$$

$$H = \left(b^\dagger b + \frac{1}{2} \right) \hbar\omega$$

$$b^\dagger b = \frac{H}{\hbar\omega} - \frac{1}{2} = N \rightarrow number\ operator$$

$$\left[b_r , b_s^\dagger \right]_- = \delta_{rs}$$

$$bb^\dagger - b^\dagger b = 1$$

$$N = b^\dagger b = \left(bb^\dagger - 1 \right)$$

$$Nb = \left(b^\dagger b \right) b = \left(bb^\dagger - 1 \right) b$$

$$Nb = bb^\dagger b - b$$

$$= bN - b$$

$$= b(N-1)$$

$$Nb|n\rangle = b(N-1)|n\rangle$$

$$Nb|n\rangle = b(n-1)|n\rangle$$

$$= (n-1)b|n\rangle$$

$b|n\rangle$ *is also an eigenvector of* N

$\rightarrow$ *belongs to eigenvalue* $(n-1)$

$$b^{\dagger}b = \frac{H}{\hbar\omega} - \frac{1}{2} = N \rightarrow number\ operator$$

$$\left[b_r, b_s^{\dagger}\right]_{-} = \delta_{rs}$$

$$bb^{\dagger} - b^{\dagger}b = 1$$

$$b|n\rangle\ is\ also\ an\ eigenvector\ of\ N$$

$$\rightarrow belongs\ to\ eigenvalue\ (n-1)$$

norm of $b|n\rangle$

$$\langle n|b^{\dagger}b|n\rangle = \langle n|N|n\rangle = n$$

normalized occupation number vectors

$$\langle n|n\rangle = 1$$

$$\langle n-1|n-1\rangle = 1$$

$$b|n\rangle = \sqrt{n}\,|n-1\rangle$$

$$b^\dagger b = \frac{H}{\hbar\omega} - \frac{1}{2} = N \rightarrow number\ operator$$

$$\left[b_r, b_s^\dagger\right]_- = \delta_{rs}$$

$$bb^\dagger - b^\dagger b = 1$$

$$bb^\dagger = 1 + b^\dagger b$$

$$Nb^\dagger = b^\dagger bb^\dagger = b^\dagger\left(bb^\dagger\right)$$

$$Nb^\dagger = b^\dagger\left(1 + b^\dagger b\right)$$

$$= b^\dagger + b^\dagger b^\dagger b$$

$$= b^\dagger (1 + N)$$

$$bb^\dagger = 1 + b^\dagger b$$

$$= N + 1$$

norm of $b^\dagger |n\rangle$

$$\langle n | bb^\dagger | n \rangle = n + 1$$

$$Nb^\dagger |n\rangle = b^\dagger (1 + N)|n\rangle$$

$$= (1 + n) b^\dagger |n\rangle$$

normalized occupation number vectors

$$\langle n | n \rangle = 1$$

$$\langle n+1 | n+1 \rangle = 1$$

$$b^\dagger |n\rangle = \sqrt{n+1}\, |n+1\rangle$$

fundamental anti − commutation rules for fermions :

$$\left[a_r, a_s^\dagger\right]_+ = \delta_{rs} \qquad \left[a_r^\dagger, a_s^\dagger\right]_+ = 0 \qquad \left[a_r, a_s\right]_+ = 0$$

$$n_s = a_s^\dagger a_s \quad \therefore \quad n_s^2 = n_s$$

a†a : Number operator

eigenvalues of n_s : 0 or 1

Number 0 'zero'

$$a^\dagger|1\rangle = 0 \qquad a|0\rangle = 0$$

a†: Creation operator

Vacuum state : No particle $|0\rangle$

a: Destruction operator

$$a^\dagger|0\rangle = |1\rangle \qquad a|1\rangle = |0\rangle$$

$$|1\rangle = a^\dagger |0\rangle$$

Ordered set:

$$a_1 < a_2 < .. < a_i < .. < a_j < .. < a_N$$

$$|n_1,..n_s,..,n_\infty\rangle = (a_1^\dagger)^{n_1}(a_2^\dagger)^{n_2}(a_3^\dagger)^{n_3}....(a_s^\dagger)^{n_s}......(a_\infty^\dagger)^{n_\infty}|0\rangle$$

eg. '3-electron system' in the lowest 3-fermion state:

$$|n_1 = 1, n_2 = 1, n_3 = 1\rangle = (a_1^\dagger)^1(a_2^\dagger)^1(a_3^\dagger)^1|0\rangle$$

i.e. $|1_1,1_2,1_3\rangle = a_1^\dagger a_2^\dagger a_3^\dagger |0\rangle$

Now,
suppose you annihilate the electron/fermion in state '2'

$$a_2|1_1,1_2,1_3\rangle = a_2 a_1^\dagger a_2^\dagger a_3^\dagger |0\rangle$$

$\therefore \quad a_2|1_1,1_2,1_3\rangle = -a_1^\dagger a_2 a_2^\dagger a_3^\dagger |0\rangle$ since $\left[a_r, a_s^\dagger\right]_+ = \delta_{rs}$

$$\therefore \quad a_2 |1_1, 1_2, 1_3\rangle = -a_1{}^\dagger a_2 a_2{}^\dagger a_3{}^\dagger |0\rangle$$ since $\left[a_r, a_s{}^\dagger\right]_+ = \delta_{rs}$

$$\therefore \quad a_2 |1_1, 1_2, 1_3\rangle = -a_1{}^\dagger \left(1 - a_2{}^\dagger a_2\right) a_3{}^\dagger |0\rangle$$

$$\therefore \quad a_2 |1_1, 1_2, 1_3\rangle = -a_1{}^\dagger a_3{}^\dagger |0\rangle + a_1{}^\dagger a_2{}^\dagger a_2 |1_3\rangle$$

$$\therefore \quad a_2 |1_1, 1_2, 1_3\rangle = -a_1{}^\dagger a_3{}^\dagger |0\rangle$$

Note the minus sign

$$\therefore \quad a_2 \left|1_1, 1_2, 1_3\right\rangle = -a_1^{\dagger} a_3^{\dagger} |0\rangle$$

Note the minus sign

$$\left|n_1, .., n_s, .., n_\infty\right\rangle = \left(a_1^{\dagger}\right)^{n_1} \left(a_2^{\dagger}\right)^{n_2} \left(a_3^{\dagger}\right)^{n_3} ....\left(a_s^{\dagger}\right)^{n_s} ......\left(a_\infty^{\dagger}\right)^{n_\infty} |0\rangle$$

Now,

suppose you annihilate the electron/fermion in state 's'

$$a_s \left|n_1, .., n_s = 1, .., n_\infty\right\rangle = a_s \left(a_1^{\dagger}\right)^{n_1} \left(a_2^{\dagger}\right)^{n_2} ....\left(a_s^{\dagger}\right)^{n_s = 1} ......\left(a_\infty^{\dagger}\right)^{n_\infty} |0\rangle$$

$$a_s \left|n_1, .., n_s, .., n_\infty\right\rangle = ?$$

What sign shall we have?

$$Ofcourse,\ if\ n_s = 0, \quad a_s \left|n_1, .., n_s = 0, .., n_\infty\right\rangle = 0$$

for $n_s = 1$ What sign shall we have?

Now,

suppose you annihilate the electron/fermion in state ‘s’

$$Ofcourse,\ \text{if}\ n_s = 0,\quad a_s \left| n_1,..,n_s = 0,..,n_\infty \right\rangle = 0$$

for $n_s = 1$

$$a_s \left| n_1,..,n_s = 1,..,n_\infty \right\rangle = a_s \left(a_1^\dagger\right)^{n_1} \left(a_2^\dagger\right)^{n_2} ....\left(a_s^\dagger\right)^{n_s=1} ......\left(a_\infty^\dagger\right)^{n_\infty} |0\rangle$$

$$\left[a_s, a_r^\dagger\right]_+ = a_s a_r^\dagger + a_r^\dagger a_s = \delta_{rs}$$

$$for\ r \neq s,\ a_s a_r^\dagger = -a_r^\dagger a_s$$

a_s can be moved to the right → pick up a minus sign.

Every one step to the right → pick up a minus sign

…….. How many steps to the right?

$$If\ \ n_s = 1, \qquad a_s\left|n_1,..,n_s=1,..,n_\infty\right\rangle = ?$$

$$a_s\left|n_1,..,n_s=1,..,n_\infty\right\rangle = a_s\left(a_1^\dagger\right)^{n_1}\left(a_2^\dagger\right)^{n_2}..\left(a_s^\dagger\right)^{n_s=1}...\left(a_\infty^\dagger\right)^{n_\infty}|0\rangle$$

$$a_s\left|n_1,..,n_s=1,..,n_\infty\right\rangle =$$

$$=(-1)^{(n_1+n_2+...+n_{s-1})}\left(a_1^\dagger\right)^{n_1}\left(a_2^\dagger\right)^{n_2}..a_s\left(a_s^\dagger\right)^{n_s=1}...\left(a_\infty^\dagger\right)^{n_\infty}|0\rangle$$

$$\left[a_s,a_r^\dagger\right]_+ = a_s a_r^\dagger + a_r^\dagger a_s = \delta_{rs}$$

$$for\ \ r=s,\ \ a_s a_s^\dagger = 1 - a_s^\dagger a_s$$

$$a_s\left|n_1,..,n_s=1,..,n_\infty\right\rangle = (-1)^{S_s}\left(a_1^\dagger\right)^{n_1}\left(a_2^\dagger\right)^{n_2}..\left[1-a_s^\dagger a_s\right]...\left(a_\infty^\dagger\right)^{n_\infty}|0\rangle$$

where $S_s = \left(n_1+n_2+...+n_{s-1}\right)$

$$a_s\left|n_1,..,n_s=1,..,n_\infty\right\rangle = (-1)^{S_s}\left|n_1,..,n_s=0,..,n_\infty\right\rangle$$

annihilation

$$n_s = 0 \quad : \quad a_s \left| n_1, .., n_s = 0, .., n_\infty \right\rangle = 0$$

$$n_s = 1 \quad : \quad a_s \left| n_1, .., n_s = 1, .., n_\infty \right\rangle = (-1)^{S_s} \left| n_1, .., n_s = 0, .., n_\infty \right\rangle$$

where $S_s = (n_1 + n_2 + ... + n_{s-1})$

creation

$$n_s = 1 \quad : \quad a_s^\dagger \left| n_1, .., n_s = 1, .., n_\infty \right\rangle = 0$$

$$n_s = 0 \quad : \quad a_s^\dagger \left| n_1, .., n_s = 0, .., n_\infty \right\rangle = (-1)^{S_s} \left| n_1, .., n_s = 1, .., n_\infty \right\rangle$$

$$n_s = 1 \quad : \quad a_s \left| n_1, .., n_s = 1, .., n_\infty \right\rangle = (-1)^{S_s} \left| n_1, .., n_s = 0, .., n_\infty \right\rangle$$

where $S_s = \left(n_1 + n_2 + ... + n_{s-1} \right)$

$$a_s^\dagger a_s \left| n_1, .., n_s = 1, .., n_\infty \right\rangle = (-1)^{S_s} a_s^\dagger \left| n_1, .., n_s = 0, .., n_\infty \right\rangle$$

$$a_s^\dagger a_s \left| n_1, .., n_s = 1, .., n_\infty \right\rangle = (-1)^{S_s} (-1)^{S_s} \left| n_1, .., n_s = 1, .., n_\infty \right\rangle$$
$$= \left| n_1, .., n_s = 1, .., n_\infty \right\rangle$$

$$a_s^\dagger a_s \left| n_1, .., n_s = 0, .., n_\infty \right\rangle = \left| n_1, .., n_s = 0, .., n_\infty \right\rangle$$

$$a_s^\dagger a_s \left| n_1, .., n_s, .., n_\infty \right\rangle = n_s \left| n_1, .., n_s, .., n_\infty \right\rangle$$

for both $n_s = 0$ and $n_s = 1$

$$n_s = 0 \quad : \quad a_s \left| n_1, .., n_s = 0, .., n_\infty \right\rangle = 0$$

$$n_s = 1 \quad : \quad a_s \left| n_1, .., n_s = 1, .., n_\infty \right\rangle = (-1)^{S_s} \left| n_1, .., n_s = 0, .., n_\infty \right\rangle$$

$$S_s = \left(n_1 + n_2 + ... + n_{s-1} \right)$$

i.e.

$$n_s = 0 \quad : \quad a_s \left| n_1, .., n_s, .., n_\infty \right\rangle = 0$$

$$n_s = 1 \quad : \quad a_s \left| n_1, .., n_s, .., n_\infty \right\rangle = (-1)^{S_s} n_s \left| n_1, .., n_s - 1, .., n_\infty \right\rangle$$

Also written, equivalently, as:

$$n_s = 0 \quad : \quad a_s \left| n_1, .., n_s, .., n_\infty \right\rangle = 0$$

$$n_s = 1 \quad : \quad a_s \left| n_1, .., n_s, .., n_\infty \right\rangle = (-1)^{S_s} \sqrt{n_s} \left| n_1, .., n_s - 1, .., n_\infty \right\rangle$$

… to make the relation look like the Boson case (except for the phase -1^{S_s})

$$S_s = (n_1 + n_2 + \ldots + n_{s-1})$$

$$n_s = 1 \quad : \quad a_s^\dagger |n_1, .., n_s = 1, .., n_\infty\rangle = 0$$

$$n_s = 0 \quad : \quad a_s^\dagger |n_1, .., n_s = 0, .., n_\infty\rangle = (-1)^{S_s} |n_1, .., n_s + 1, .., n_\infty\rangle$$

i.e.

$$n_s = 1 \quad : \quad a_s^\dagger |n_1, .., n_s = 1, .., n_\infty\rangle = 0$$

$$n_s = 0 \quad : \quad a_s^\dagger |n_1, .., n_s = 0, .., n_\infty\rangle = (-1)^{S_s} (1 - n_s) |n_1, .., n_s + 1, .., n_\infty\rangle$$

Also written, equivalently, as:

$$n_s = 1 \quad : \quad a_s^\dagger |n_1, .., n_s = 1, .., n_\infty\rangle = 0$$

$$n_s = 0 \quad : \quad a_s^\dagger |n_1, .., n_s = 0, .., n_\infty\rangle = (-1)^{S_s} \sqrt{n_s + 1} |n_1, .., n_s + 1, .., n_\infty\rangle$$

… to make the relation look like the Boson case (except for the phase -1^{S_s})

Many-Electron Hamiltonian
in the
First Quantization notation

(for *both* Fermions/Bosons)

$$H = H_0 + H'$$

$$= \sum_{i=1}^{N} f(q_i) + \frac{1}{2} \sum_{i=1}^{N} \sum_{\substack{j=1 \\ i \neq j}}^{N} \mathrm{v}(q_i, q_j)$$

How shall we write the Many-Electron Hamiltonian
in the
SECOND QUANTIZATION notation*?*

$$i\hbar\frac{\partial}{\partial t}\Psi(x_1,x_2,...,x_N,t)=H\Psi(x_1,x_2,...,x_N,t)$$

.. *from previous class*:

(for *both* Fermions/Bosons)

$$\Psi(x_1,x_2,..,x_N,t)=\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C(E_1',E_2',..,E_N',t)\psi_{E_1'}(x_1)\psi_{E_2'}(x_2)..\psi_{E_N'}(x_N)$$

$FW\ Eq.1.3$

multiply the Schrodinger equation by $\psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger$

for a fixed set $\{E_1,E_2,..E_N\}$

Details in previous class

$$\psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times i\hbar\frac{\partial}{\partial t}\Psi(x_1,x_2,...,x_N,t)=$$

$$=\psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times H\Psi(x_1,x_2,...,x_N,t)$$

Now, integrate over all coordinates

$$i\hbar\int dx_1\int dx_2..\int dx_N\ \ \psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times\frac{\partial}{\partial t}\Psi(x_1,x_2,...,x_N,t)=$$

$$=\int dx_1\int dx_2..\int dx_N\ \ \psi_{E_1}(x_1)^\dagger\psi_{E_2}(x_2)^\dagger..\psi_{E_N}(x_N)^\dagger\times H\Psi(x_1,x_2,...,x_N,t)$$

$$i\hbar\int dx_1\int dx_2..\int dx_N \left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger \psi_{E_2}(x_2)^\dagger ..\psi_{E_N}(x_N)^\dagger \times \\ \frac{\partial}{\partial t}\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'} C(E_1',E_2',..,E_N',t)\psi_{E_1'}(x_1)\psi_{E_2'}(x_2)..\psi_{E_N'}(x_N)\end{array}\right] =$$

$$=\int dx_1\int dx_2..\int dx_N \left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger \psi_{E_2}(x_2)^\dagger ..\psi_{E_N}(x_N)^\dagger \times \\ H\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'} C(E_1',E_2',..,E_N',t)\psi_{E_1'}(x_1)\psi_{E_2'}(x_2)..\psi_{E_N'}(x_N)\end{array}\right]$$

l.h.s.

Details in previous class

$$\int dx_k \;\; \psi_{E_i}(x_k)^\dagger \psi_{E_i'}(x_k) = \delta_{E_i E_i'}$$

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) =$$

$$=\int dx_1\int dx_2..\int dx_N \left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger \psi_{E_2}(x_2)^\dagger ..\psi_{E_N}(x_N)^\dagger \times \\ H\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'} C(E_1',E_2',..,E_N',t)\psi_{E_1'}(x_1)\psi_{E_2'}(x_2)..\psi_{E_N'}(x_N)\end{array}\right]$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right)=$$

$$=\int dx_1\int dx_2..\int dx_N\left[\begin{array}{l}\psi_{E_1}\left(x_1\right)^{\dagger}\psi_{E_2}\left(x_2\right)^{\dagger}..\psi_{E_N}\left(x_N\right)^{\dagger}\times\\ H\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C\left(E_1',E_2',..,E_N',t\right)\psi_{E_1'}\left(x_1\right)\psi_{E_2'}\left(x_2\right)..\psi_{E_N'}\left(x_N\right)\end{array}\right]$$

Details in previous class

$$H=\left\{\sum_{k=1}^{N}T(x_k)+\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1\\ k\neq l}}^{N}V(x_k,x_l)\right\}$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right)=$$

$$=\sum_{E_1'}\sum_{E_2'}..\sum_{E_N'}C\left(E_1',E_2',..,E_N',t\right)\int dx_1\int dx_2..\int dx_N\left[\begin{array}{l}\psi_{E_1}\left(x_1\right)^{\dagger}\psi_{E_2}\left(x_2\right)^{\dagger}..\psi_{E_N}\left(x_N\right)^{\dagger}\times\\ \left\{\sum_{k=1}^{N}T(x_k)+\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1\\ k\neq l}}^{N}V(x_k,x_l)\right\}\psi_{E_1'}\left(x_1\right)\psi_{E_2'}\left(x_2\right)..\psi_{E_N'}\left(x_N\right)\end{array}\right]$$

$$i\hbar \frac{\partial}{\partial t} C(E_1, E_2, .., E_N, t) =$$

$$= \sum_{E_1'} \sum_{E_2'} .. \sum_{E_N'} C(E_1', .., E_N', t) \int dx_1 .. \int dx_N \begin{bmatrix} \psi_{E_1}(x_1)^\dagger .. \psi_{E_N}(x_N)^\dagger \times \\ \left\{ \sum_{k=1}^{N} T(x_k) \right\} \psi_{E_1'}(x_1) .. \psi_{E_N'}(x_N) \end{bmatrix} +$$

K.E. term

$$+ \sum_{E_1'} \sum_{E_2'} .. \sum_{E_N'} C(E_1', .., E_N', t) \int dx_1 .. \int dx_N \begin{bmatrix} \psi_{E_1}(x_1)^\dagger .. \psi_{E_N}(x_N)^\dagger \times \\ \left\{ \frac{1}{2} \sum_{k=1}^{N} \sum_{\substack{l=1 \\ k \neq l}}^{N} V(x_k, x_l) \right\} \psi_{E_1'}(x_1) .. \psi_{E_N'}(x_N) \end{bmatrix}$$

P.E. term

Details in previous class

Integration of the one-particle terms over independent degrees of freedom

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) =$$

$$= \sum_{E_1'} ..\sum_{E_N'} \sum_{k=1}^{N} \left\{ \begin{aligned} & C(E_1',..,E_N',t)\times \\ & \times\int dx_k \psi_{E_k}(x_k)^\dagger \{T(x_k)\} \psi_{E_k'}(x_k)\times \\ & \times\int dx_1 \psi_{E_1}(x_1)^\dagger \psi_{E_1'}(x_1)..\times \\ & \times\int dx_N \psi_{E_N}(x_N)^\dagger \psi_{E_N'}(x_N) \end{aligned} \right\} +$$

$$+\sum_{E_1'} ..\sum_{E_N'} C(E_1',..,E_N',t)\int dx_1..\int dx_N \left[\begin{aligned} & \psi_{E_1}(x_1)^\dagger..\psi_{E_N}(x_N)^\dagger\times \\ & \left\{ \frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1 \\ k\neq l}}^{N} V(x_k,x_l) \right\} \psi_{E_1'}(x_1)..\psi_{E_N'}(x_N) \end{aligned} \right]$$

Details in previous class

Orthogonality and summation over E_1' etc.

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) =$$

$$= \sum_{E_1'}..\sum_{E_N'}\sum_{k=1}^{N} C(E_1',..,E_N',t)\int dx_k \psi_{E_k}(x_k)^\dagger \{T(x_k)\}\psi_{E_k'}(x_k)\int dx_1\psi_{E_1}(x_1)^\dagger\psi_{E_1'}(x_1)..\int dx_N\psi_{E_N}(x_N)^\dagger\psi_{E_N'}(x_N) +$$

$$+\sum_{E_1'}..\sum_{E_N'} C(E_1',..,E_N',t)\int dx_1..\int dx_N \left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger..\psi_{E_N}(x_N)^\dagger\times \\ \left\{\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1\\k\neq l}}^{N} V(x_k,x_l)\right\}\psi_{E_1'}(x_1)..\psi_{E_N'}(x_N)\end{array}\right]$$

Orthogonality and summation over E_1' etc.

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) = \sum_{E_k'}\sum_{k=1}^{N} C(E_1,..,E_k',..,E_N,t)\boxed{\int dx_k\psi_{E_k}(x_k)^\dagger T(x_k)\psi_{E_k'}(x_k)}+$$

E_k' appears once extra and E_k appears once less.

$$+\sum_{E_1'}..\sum_{E_N'} C(E_1',..,E_N',t)\int dx_1..\int dx_N \left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger..\psi_{E_N}(x_N)^\dagger\times \\ \left\{\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1\\k\neq l}}^{N} V(x_k,x_l)\right\}\psi_{E_1'}(x_1)..\psi_{E_N'}(x_N)\end{array}\right]$$

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) = \sum_{E_k'}\sum_{k=1}^{N} C(E_1,..,\underbrace{E_k'}_{},..,E_N,t)\int dx_k \psi_{E_k}(x_k)^\dagger T(x_k)\psi_{E_k'}(x_k) +$$

$$+\sum_{E_1'}..\sum_{E_N'} C(E_1',..,E_N',t)\int dx_1..\int dx_N \left[\begin{array}{l}\psi_{E_1}(x_1)^\dagger..\psi_{E_N}(x_N)^\dagger \times \\ \left\{\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1\\ \boxed{k\neq l}}}^{N} V(x_k,x_l)\right\}\psi_{E_1'}(x_1)..\psi_{E_N'}(x_N)\end{array}\right]$$

In the K.E. term:

E_k' appears once extra and *E_k* appears once less.

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) = \sum_{E_{k'}}\sum_{k=1}^{N}\left\{\begin{array}{l}C(E_1,..,E_{k-1},E_{k'},E_{k+1},..E_N,t)\times \\ \times\int dx_k \psi_{E_k}(x_k)^\dagger T(x_k)\psi_{E_{k'}}(x_k)\end{array}\right\}+$$

FW Eq.1.4

$$+\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1\\ \boxed{k\neq l}}}^{N}\sum_{E_{k'}}\sum_{E_{l'}}\left\{\begin{array}{l}C(E_1,..,E_{k-1},E_{k'},E_{k+1},..,E_{l-1},E_{l'},E_{l+1},..E_N,t)\times \\ \times\int dx_k\int dx_l \psi_{E_k}(x_k)^\dagger \psi_{E_l}(x_l)^\dagger V(x_k,x_l)\psi_{E_{k'}}(x_k)\psi_{E_{l'}}(x_l)\end{array}\right\}$$

In the P.E. term:

E_k' & E_l' appear once extra, and *E_k & E_l* appear once less.

$$f\left(n_1, n_2, ..n_i, .., n_j, .., ...n_\infty, t\right) \equiv C\left(E_1 < E_2 < .. < E_i < .. < E_j < .. < E_N, t\right)$$

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) = \sum_{E_{k'}}\sum_{k=1}^{N}\langle E_k|T|E_{k'}\rangle C(E_1,..,E_{k-1},E_{k'},E_{k+1},..E_N,t)+$$

$$+\frac{1}{2}\sum_{k=1}^{N}\sum_{\substack{l=1 \\ k\neq l}}^{N}\sum_{E_{k'}}\sum_{E_{l'}}\langle E_kE_l|V|E_{k'}E_{l'}\rangle C(E_1,..,E_{k-1},E_{k'},E_{k+1},..,E_{l-1},E_{l'},E_{l+1},..E_N,t)$$

In the K.E. term:

E_k' appears once extra and E_k appears once less.

In the P.E. term:

E_k' & E_l' appear once extra, and E_k & E_l appear once less.

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) =$$

$$=\sum_{E_{k'}}\sum_{E_k}\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\langle E_k|T|E_{k'}\rangle C(E_1,..,E_{k-1},E_{k'},E_{k+1},..E_N,t)+$$

$$+\frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{l'}}\left[\begin{array}{l}\left\{\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\right\}\left\{\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\right\} \\ \left\{\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\right\}\left\{\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\right\} \\ \left\{\begin{array}{l}\langle E_kE_l|V|E_{k'}E_{l'}\rangle\times \\ C(E_1,..,E_{k-1},E_{k'},E_{k+1},..,E_{l-1},E_{l'},E_{l+1},..E_N,t)\end{array}\right\}\end{array}\right]$$

$$i\hbar\frac{\partial}{\partial t}C(E_1,E_2,..,E_N,t) =$$

$$=\sum_{E_{k'}}\sum_{E_k}\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\langle E_k|T|E_{k'}\rangle C(E_1,..,E_{k-1},E_{k'},E_{k+1},..E_N,t)+$$

$$+\frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{l'}}\left[\begin{matrix}\left\{\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\right\}\left\{\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\right\}\\ \left\{\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\right\}\left\{\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\right\}\\ \left\{\begin{matrix}\langle E_kE_l|V|E_{k'}E_{l'}\rangle\times\\ C(E_1,..,E_{k-1},E_{k'},E_{k+1},..,E_{l-1},E_{l'},E_{l+1},..E_N,t)\end{matrix}\right\}\end{matrix}\right]$$

all information about which one-electron states are occupied is contained in a coefficient:

$f(n_1,n_2,..n_i,..,n_j,..,....n_\infty,t)$ where $n_i=0$ <u>or</u> 1

$$f(n_1,n_2,..n_i,..,n_j,..,....n_\infty,t)\equiv C(E_1<E_2<..<E_i<..<E_j<..<E_N,t)$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right) \quad =$$

$$=\sum_{E_{k'}}\sum_{E_k}\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\left\langle E_k\left|T\right|E_{k'}\right\rangle C\left(E_1,..,E_{k-1},E_{k'},E_{k+1},..E_N,t\right)+$$

$$+\frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{l'}}\left[\begin{array}{l}\left\{\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\right\}\left\{\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\right\}\\ \left\{\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\right\}\left\{\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\right\}\\ \left\{\begin{array}{l}\left\langle E_kE_l\left|V\right|E_{k'}E_{l'}\right\rangle\times\\ C\left(E_1,..,E_{k-1},E_{k'},E_{k+1},..,E_{l-1},E_{l'},E_{l+1},..E_N,t\right)\end{array}\right\}\end{array}\right]$$

In the coefficient

$$C\left(E_1,..,E_{k-1},E_{k'},E_{k+1},..E_N,t\right)$$

If $E_{k'}<E_k$, *then we need an extra phase factor*

$$(-1)^{n_{E_{k'+1}}}(-1)^{n_{E_{k'+2}}}...(-1)^{n_{E_{k-1}}}=(-1)^{n_{E_{k'+1}}+n_{E_{k'+2}}.....+n_{E_{k-1}}}$$

-depending on how many interchanges are needed to get it in the proper order.

If $E_{k'}>E_k$, *then we need an extra phase factor*

$$(-1)^{n_{E_{k+1}}}(-1)^{n_{E_{k+2}}}...(-1)^{n_{E_{k'-1}}}=(-1)^{n_{E_{k+1}}+n_{E_{k+2}}+.....+n_{E_{k'-1}}}$$

$$i\hbar\frac{\partial}{\partial t}C\left(E_1,E_2,..,E_N,t\right) \quad =$$

$$=\sum_{E_{k'}}\sum_{E_k}\begin{bmatrix}\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\\ \sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\end{bmatrix}(-1)^{n_{E_{k'+1}}+..+n_{E_{k-1}}}\left\langle E_k\left|T\right|E_{k'}\right\rangle C\left(E_1,..,E_{k-1},E_{k'},E_{k+1},..E_N,t\right)+$$

$$+\frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{l'}}\begin{bmatrix}\left\{\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\right\}\left\{\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\right\}\\ \left\{\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\right\}\left\{\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\right\}\\ \left\{\begin{array}{l}\begin{bmatrix}(-1)^{n_{E_{k'+1}}+..+n_{E_{k-1}}}\times\\ (-1)^{n_{E_{l'+1}}+..+n_{E_{l-1}}}\end{bmatrix}\left\langle E_kE_l\left|V\right|E_{k'}E_{l'}\right\rangle\times\\ C\left(E_1,..,E_{k-1},E_{k'},E_{k+1},..,E_{l-1},E_{l'},E_{l+1},..E_N,t\right)\end{array}\right\}\end{bmatrix}$$

$$f\left(n_1,n_2,..n_i,..,n_j,..,....n_\infty,t\right)\equiv C\left(E_1<E_2<..<E_i<..<E_j<..<E_N,t\right)$$

$$i\hbar\frac{\partial}{\partial t} f\left(n_1,n_2,..,n_{E_k},..,n_{E_{k'}},..,n_{E_l},..,n_{E_{l'}},....n_\infty,t\right) =$$

$$=\sum_{E_{k'}}\sum_{E_k}\begin{bmatrix}\sqrt{n_{E_k}+1}\delta_{n_{E_k},0}\\ \sqrt{n_{E_{k'}}}\delta_{n_{E_{k'}},1}\end{bmatrix}(-1)^{n_{E_{k'}+1}+..+n_{E_{k-1}}}\langle E_k|T|E_{k'}\rangle f\left(n_1,n_2,..n_i,..,n_{E_k}+1,..,n_{E_{k'}}-1,..n_\infty,t\right)+$$

$$+\frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{l'}}\begin{bmatrix}\left\{\sqrt{n_{E_k}+1}\delta_{n_{E_k},0}\right\}\left\{\sqrt{n_{E_{k'}}}\delta_{n_{E_{k'}},1}\right\}\\ \left\{\sqrt{n_{E_l}+1}\delta_{n_{E_l},0}\right\}\left\{\sqrt{n_{E_{l'}}}\delta_{n_{E_{l'}},1}\right\}\\ \left\{\begin{array}{l}\begin{bmatrix}(-1)^{n_{E_{k'}+1}+..+n_{E_{k-1}}}\times\\ (-1)^{n_{E_{l'}+1}+..+n_{E_{l-1}}}\end{bmatrix}\langle E_kE_l|V|E_{k'}E_{l'}\rangle\times\\ f\left(n_1,n_2,..n_i,..,n_{E_k}+1,..,n_{E_{k'}}-1,..,n_{E_l}+1,..,n_{E_{l'}}-1,..n_\infty,t\right)\end{array}\right\}\end{bmatrix}$$

We used:

$$f\left(n_1,n_2,..n_i,..,n_j,..,....n_\infty,t\right)\equiv C\left(E_1<E_2<..<E_i<..<E_j<..<E_N,t\right)$$

$$i\hbar\frac{\partial}{\partial t} f\left(n_1, n_2, .., n_{E_k}, .., n_{E_{k'}}, .., n_{E_l}, .., n_{E_{l'}}, ...n_\infty, t\right) =$$

$$= \sum_{E_{k'}} \sum_{E_k} \begin{bmatrix} \sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0} \\ \sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1} \end{bmatrix} (-1)^{n_{E_{k'+1}}+..+n_{E_{k-1}}} \langle E_k|T|E_{k'}\rangle f\left(n_1, n_2, ..n_i, .., n_{E_k}+1, .., n_{E_{k'}}-1, ..n_\infty, t\right) +$$

$$+\frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{l'}} \begin{bmatrix} \left\{\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\right\}\left\{\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\right\} \\ \left\{\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\right\}\left\{\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\right\} \\ \left\{ \begin{bmatrix} (-1)^{n_{E_{k'+1}}+..+n_{E_{k-1}}} \times \\ (-1)^{n_{E_{l'+1}}+..+n_{E_{l-1}}} \end{bmatrix} \langle E_k E_l|V|E_{k'}E_{l'}\rangle \times \\ f\left(n_1, n_2, ..n_i, .., n_{E_k}+1, .., n_{E_{k'}}-1, .., n_{E_l}+1, .., n_{E_{l'}}-1, ..n_\infty, t\right) \right\} \end{bmatrix}$$

$$(-1)^{n_{E_{k'+1}}+..+n_{E_{k-1}}} = (-1)^{S_{E_k}-S_{E_{k'}}}$$

$(-1)^{S_s}$ has $S_s = \left(n_1 + n_2 + \ldots + n_{s-1}\right)$

$$(-1)^{n_{E_{k'+1}}+..+n_{E_{k-1}}} \times (-1)^{n_{E_{l'+1}}+..+n_{E_{l-1}}} = (-1)^{n_{E_k}-n_{E_{k'}}+n_{E_l}-n_{E_{l'}}}$$

$$i\hbar\frac{\partial}{\partial t} f\left(n_1, n_2, .., n_{E_k}, .., n_{E_{k'}}, .., n_{E_l}, .., n_{E_{l'}}, ...n_\infty, t\right) =$$

$$= \sum_{E_{k'}} \sum_{E_k} \begin{bmatrix} \sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0} \\ \sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1} \end{bmatrix} (-1)^{S_{E_k}-S_{E_{k'}}} \langle E_k|T|E_{k'}\rangle\, f\left(n_1, n_2, ..n_i, ., n_{E_k}+1, .., n_{E_{k'}}-1, ..n_\infty, t\right) +$$

$$+\frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{l'}} \begin{bmatrix} \left\{\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\right\}\left\{\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\right\} \\ \left\{\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\right\}\left\{\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\right\} \\ \left\{ \begin{array}{l} (-1)^{n_{E_k}-n_{E_{k'}}+n_{E_l}-n_{E_{l'}}} \langle E_k E_l|V|E_{k'} E_{l'}\rangle \times \\ f\left(n_1, n_2, ..n_i, ., n_{E_k}+1, .., n_{E_{k'}}-1, .., n_{E_l}+1, .., n_{E_{l'}}-1, ..n_\infty, t\right) \end{array} \right\} \end{bmatrix}$$

Above, we have used:

$$(-1)^{n_{E_{k'+1}}+..+n_{E_{k-1}}} = (-1)^{S_{E_k}-S_{E_{k'}}}$$

$$(-1)^{n_{E_{k'+1}}+..+n_{E_{k-1}}} \times (-1)^{n_{E_{l'+1}}+..+n_{E_{l-1}}} = (-1)^{n_{E_k}-n_{E_{k'}}+n_{E_l}-n_{E_{l'}}}$$

$$i\hbar\frac{\partial}{\partial t} f\left(n_1, n_2, .., n_{E_k}, .., n_{E_{k'}}, .., n_{E_l}, .., n_{E_{l'}}, ...n_\infty, t\right) =$$

$$= \sum_{E_{k'}} \sum_{E_k} \begin{bmatrix} \sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0} \\ \sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1} \end{bmatrix} (-1)^{S_{E_k}-S_{E_{k'}}} \langle E_k|T|E_{k'}\rangle f\left(n_1, n_2, ..n_i, ., n_{E_k}+1, .., n_{E_{k'}}-1, ..n_\infty, t\right) +$$

$$+ \frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{l'}} \begin{bmatrix} \left\{\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\right\}\left\{\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\right\} \\ \left\{\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\right\}\left\{\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\right\} \\ \left\{ \begin{matrix} (-1)^{n_{E_k}-n_{E_{k'}}+n_{E_l}-n_{E_{l'}}} \langle E_k E_l|V|E_{k'} E_{l'}\rangle \times \\ f\left(n_1, n_2, ..n_i, ., n_{E_k}+1, .., n_{E_{k'}}-1, .., n_{E_l}+1, .., n_{E_{l'}}-1, ..n_\infty, t\right) \end{matrix} \right\} \end{bmatrix}$$

$$\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}(-1)^{S_{E_k}-S_{E_{k'}}}\left|n_1 n_2 ... n_{E_k}+1 ... n_{E_{k'}}-1 ..... n_\infty\right\rangle =$$

$$= a^\dagger_{E_k} a_{E_{k'}}\left|n_1 n_2 ..... n_\infty\right\rangle$$

$$i\hbar\frac{\partial}{\partial t} f\left(n_1,n_2,..,n_{E_k},..,n_{E_{k'}},..,n_{E_l},..,n_{E_{l'}},....n_\infty,t\right) =$$

$$= \sum_{E_{k'}}\sum_{E_k}\begin{bmatrix}\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0} \\ \sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\end{bmatrix}(-1)^{S_{E_k}-S_{E_{k'}}}\langle E_k|T|E_{k'}\rangle f\left(n_1,n_2,..n_i,..,n_{E_k}+1,..,n_{E_{k'}}-1,..n_\infty,t\right)+$$

$$+\frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{l'}}\left[\begin{matrix}\left\{\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\right\}\left\{\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\right\} \\ \left\{\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\right\}\left\{\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\right\} \\ \left\{(-1)^{n_{E_k}-n_{E_{k'}}+n_{E_l}-n_{E_{l'}}} \times \langle E_k E_l|V|E_{k'}E_{l'}\rangle \times f\left(n_1,n_2,..n_i,..,n_{E_k}+1,..,n_{E_{k'}}-1,..,n_{E_l}+1,..,n_{E_{l'}}-1,..n_\infty,t\right)\right\}\end{matrix}\right]$$

$$\left[\begin{matrix}\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\times(-1)^{n_{E_k}-n_{E_{k'}}+n_{E_l}-n_{E_{l'}}}\times \\ \times\left|n_1 n_2 ... n_{E_k}+1..n_{E_{k'}}-1..n_{E_l}+1..n_{E_{l'}}-1...n_\infty\right\rangle\end{matrix}\right]=$$

$$= a^\dagger_{E_k} a_{E_{k'}} a^\dagger_{E_l} a_{E_{l'}}\left|n_1 n_2.....n_\infty\right\rangle$$

$$i\hbar\frac{\partial}{\partial t} f\left(n_1,n_2,..,n_{E_k},..,n_{E_{k'}},..,n_{E_l},..,n_{E_{l'}},....n_\infty,t\right) =$$

$$=\sum_{E_{k'}}\sum_{E_k}\begin{bmatrix}\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\\ \sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\end{bmatrix}(-1)^{S_{E_k}-S_{E_{k'}}}\left\langle E_k\left|T\right|E_{k'}\right\rangle f\left(n_1,n_2,..n_i,..,n_{E_k}+1,..,n_{E_{k'}}-1,..n_\infty,t\right)+$$

$$+\frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{l'}}\begin{bmatrix}\left\{\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\right\}\left\{\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\right\}\\ \left\{\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\right\}\left\{\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\right\}\\ \left\{\begin{matrix}(-1)^{n_{E_k}-n_{E_{k'}}+n_{E_l}-n_{E_{l'}}}\left\langle E_kE_l\left|V\right|E_{k'}E_{l'}\right\rangle\times\\ f\left(n_1,n_2,..n_i,..,n_{E_k}+1,..,n_{E_{k'}}-1,..,n_{E_l}+1,..,n_{E_{l'}}-1,..n_\infty,t\right)\end{matrix}\right\}\end{bmatrix}$$

We now use these relations in the above:

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$$\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}(-1)^{S_{E_k}-S_{E_{k'}}}\left|n_1n_2...n_{E_k}+1...n_{E_{k'}}-1....n_\infty\right\rangle=$$

$$=a^\dagger_{E_k}a_{E_{k'}}\left|n_1n_2.....n_\infty\right\rangle$$

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$$\left[\begin{matrix}\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\times(-1)^{n_{E_k}-n_{E_{k'}}+n_{E_l}-n_{E_{l'}}}\times\\ \times\left|n_1n_2...n_{E_k}+1..n_{E_{k'}}-1..n_{E_l}+1..n_{E_{l'}}-1...n_\infty\right\rangle\end{matrix}\right]=$$

$$=a^\dagger_{E_k}a_{E_{k'}}a^\dagger_{E_l}a_{E_{l'}}\left|n_1n_2.....n_\infty\right\rangle$$

$$i\hbar\frac{\partial}{\partial t} f\left(n_1,n_2,..,n_{E_k},..,n_{E_{k'}},..,n_{E_l},..,n_{E_{l'}},....n_\infty,t\right) =$$

$$= \sum_{E_{k'}}\sum_{E_k}\begin{bmatrix}\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\\ \sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\end{bmatrix}(-1)^{S_{E_k}-S_{E_{k'}}}\langle E_k|T|E_{k'}\rangle\, f\left(n_1,n_2,..n_i,..,n_{E_k}+1,..,n_{E_{k'}}-1,..n_\infty,t\right)+$$

$$+\frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{l'}}\begin{bmatrix}\left\{\sqrt{n_{E_k}+1}\,\delta_{n_{E_k},0}\right\}\left\{\sqrt{n_{E_{k'}}}\,\delta_{n_{E_{k'}},1}\right\}\\ \left\{\sqrt{n_{E_l}+1}\,\delta_{n_{E_l},0}\right\}\left\{\sqrt{n_{E_{l'}}}\,\delta_{n_{E_{l'}},1}\right\}\\ \left\{\begin{matrix}(-1)^{n_{E_k}-n_{E_{k'}}+n_{E_l}-n_{E_{l'}}}\langle E_kE_l|V|E_{k'}E_{l'}\rangle\times\\ f\left(n_1,n_2,..n_i,..,n_{E_k}+1,..,n_{E_{k'}}-1,..,n_{E_l}+1,..,n_{E_{l'}}-1,..n_\infty,t\right)\end{matrix}\right\}\end{bmatrix}$$

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle =$$

$$=\begin{bmatrix}\sum_{E_k}\sum_{E_{k'}} a^\dagger_{E_k}a_{E_{k'}}\langle E_k|T|E_{k'}\rangle+\\ +\frac{1}{2}\sum_{E_k}\sum_{E_l}\sum_{E_{k'}}\sum_{E_{k'}} a^\dagger_{E_k}a_{E_{k'}}a^\dagger_{E_l}a_{E_{l'}}\langle E_k E_l|V|E_{k'}E_{l'}\rangle\end{bmatrix}|\Psi(t)\rangle$$

$$i\hbar \frac{\partial}{\partial t}\left|\Psi(t)\right\rangle =$$

$$= \left[\begin{array}{l} \sum_{E_k} \sum_{E_{k'}} a_{E_k}^{\dagger} a_{E_{k'}} \left\langle E_k \right| T \left| E_{k'} \right\rangle + \\ + \frac{1}{2} \sum_{E_k} \sum_{E_l} \sum_{E_{k'}} \sum_{E_{k'}} a_{E_k}^{\dagger} a_{E_{k'}} a_{E_l}^{\dagger} a_{E_{l'}} \left\langle E_k E_l \right| V \left| E_{k'} E_{l'} \right\rangle \end{array} \right] \left|\Psi(t)\right\rangle$$

$$E_k, E_l, E_{k'}, E_{l'} \xrightarrow[\text{respectively by}]{\text{replace}} r,s,t,u$$

$$i\hbar \frac{\partial}{\partial t}\left|\Psi(t)\right\rangle =$$

$$= \left[\sum_r \sum_s a_r^{\dagger} a_s \langle r|T|s\rangle + \frac{1}{2} \sum_r \sum_s \sum_t \sum_u a_r^{\dagger} a_t a_s^{\dagger} a_u \langle rs|V|tu\rangle \right] \left|\Psi(t)\right\rangle$$

$$H = \sum_r \sum_s a_r^{\dagger} a_s \langle r|T|s\rangle + \frac{1}{2} \sum_r \sum_s \sum_t \sum_u a_r^{\dagger} a_t a_s^{\dagger} a_u \langle rs|V|tu\rangle$$

$$i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle = \left[\sum_r\sum_s a_r^\dagger a_s \langle r|T|s\rangle + \frac{1}{2}\sum_r\sum_s\sum_t\sum_u a_r^\dagger a_t a_s^\dagger a_u \langle rs|V|tu\rangle\right]|\Psi(t)\rangle$$

$$H = \sum_r\sum_s a_r^\dagger a_s \langle r|T|s\rangle + \frac{1}{2}\sum_r\sum_s\sum_t\sum_u a_r^\dagger a_t a_s^\dagger a_u \langle rs|V|tu\rangle$$

$$a_r^\dagger \underline{a_t a_s^\dagger} a_u = -a_r^\dagger a_s^\dagger \underline{a_t a_u} = a_r^\dagger a_s^\dagger a_u a_t$$

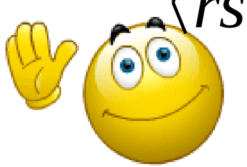
$$H = \sum_r\sum_s a_r^\dagger a_s \langle r|T|s\rangle + \frac{1}{2}\sum_r\sum_s\sum_t\sum_u a_r^\dagger a_s^\dagger a_u a_t \langle rs|V|tu\rangle$$

$$H = \sum_r\sum_s a_r^\dagger \langle r|T|s\rangle a_s + \frac{1}{2}\sum_r\sum_s\sum_t\sum_u a_r^\dagger a_s^\dagger \langle rs|V|\underline{tu}\rangle \underline{a_u a_t}$$

...Eq.1.60 / F & W / p.18

Note: ↑Order↑

$$\langle rs|V|tu\rangle = \int dq_1 \int dq_2 \phi_r^*(q_1)\phi_s^*(q_2) V(q_1,q_2)\phi_t(q_1)\phi_u(q_2)$$



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