Second quantization

- Motivation:
  - Slater determinants tedious to work with
  - Relevant operators change only the quantum numbers of one or two particles (and in exceptional cases three)
- Consider states that are labeled by the # of particles occupying sp states ⇒ occupation number representation
- Allow states in CVS with different # of particles ⇒ Fock space
- Includes new state: the vacuum $|0\rangle$
  - all sp states $\{|\alpha\rangle\}$
  - all antisymmetric two-particle (tp) states $\{|\alpha_1\alpha_2\rangle\}$
  - ..
  - all antisymmetric N-particle states $\{|\alpha_1\alpha_2...\alpha_N\rangle\}$
  - up to infinite number of particles .....

Alternative writing

- Vacuum state $$|0\rangle = \underset{\alpha_1\alpha_2...}{|0\ 0...}\ \underset{\alpha_\infty}{0\rangle}$$
- Sp state $$|\alpha_i\rangle = |0\ 0\ ...0\ \underset{\alpha_i}{1}\ 0...0\rangle$$
- Tp state $$|\alpha_i\alpha_j\rangle = |0\ 0\ ...0\ \underset{\alpha_i}{1}\ 0...0\ \underset{\alpha_j}{1}\ 0...0\rangle$$
- etc.
- Use ordered states $$\sum_{N=0}^{\infty} \sum_{\alpha_1\alpha_2..\alpha_N}^{ordered} |\alpha_1\alpha_2...\alpha_N\rangle \langle\alpha_1\alpha_2...\alpha_N| = 1$$
- Introduce new operator in Fock space $a_\alpha^\dagger$

Particle addition (creation) operator

- Definition $a_\alpha^\dagger \left|\alpha_1\alpha_2...\alpha_N\right\rangle \equiv \left|\alpha\alpha_1\alpha_2...\alpha_N\right\rangle$
- Takes an antisymmetric N-particle state and turns it into an antisymmetric N+1-particle state with α occupied!!!!
- Note:
  - $\alpha = \alpha_i$ ⇒ not a state
  - $\alpha \neq \alpha_i$ ⇒ i=1,...,N new state (may require ordering)
- Acts on any state
- Including

$$a_\alpha^\dagger \left|0\right\rangle = \left|\alpha\right\rangle$$

$$a_\alpha^\dagger \left|\beta\right\rangle = \left|\alpha\beta\right\rangle$$

- and
- etc.
- What about the adjoint operator a_α ?

Particle removal (destruction) operator

- Action of adjoint operator?

$$a_\alpha |\alpha_1\alpha_2...\alpha_N\rangle = \sum_{M=0}^{\infty} \sum_{\alpha_1'\alpha_2'..\alpha_M'}^{ordered} |\alpha_1'\alpha_2'..\alpha_M'\rangle \langle\alpha_1'\alpha_2'..\alpha_M'| a_\alpha |\alpha_1\alpha_2..\alpha_N\rangle$$

$$= \sum_{M=0}^{\infty} \sum_{\alpha_1'\alpha_2'..\alpha_M'}^{ordered} |\alpha_1'\alpha_2'..\alpha_M'\rangle \langle\alpha_1\alpha_2..\alpha_N| a_\alpha^\dagger |\alpha_1'\alpha_2'..\alpha_M'\rangle^*$$

$$= \sum_{M=0}^{\infty} \sum_{\alpha_1'\alpha_2'..\alpha_M'}^{ordered} |\alpha_1'\alpha_2'..\alpha_M'\rangle \langle\alpha_1\alpha_2..\alpha_N|\alpha\alpha_1'\alpha_2'..\alpha_M'\rangle^*$$

- Consider once α placed in the correct location ⇒ $(-1)^{i-1}$

$$\langle\alpha_1\alpha_2...\alpha_N|\alpha_1'\alpha_2'...\alpha\alpha_i'...\alpha_M'\rangle = \delta_{\alpha_1,\alpha_1'}\delta_{\alpha_2,\alpha_2'}...\delta_{\alpha_i,\alpha}\delta_{\alpha_{i+1},\alpha_i'}...\delta_{\alpha_N,\alpha_{N-1}'}$$

- So $a_\alpha |\alpha_1\alpha_2...\alpha_N\rangle = (-1)^{i-1} |\alpha_1\alpha_2...\alpha_{i-1}\alpha_{i+1}...\alpha_N\rangle$ if $\alpha = \alpha_i$
- or $a_\alpha |\alpha_1\alpha_2...\alpha_N\rangle = 0$ if $\alpha \neq \alpha_i, i = 1, ..., N$
- Example: $a_\alpha |0\rangle = 0$ Note: again antisymmetric state!

Fermion anticommutation relations

$$\{a_\alpha, a_\beta^\dagger\} = a_\alpha a_\beta^\dagger + a_\beta^\dagger a_\alpha = \delta_{\alpha,\beta}$$

$$\{a_\alpha, a_\beta\} = \{a_\alpha^\dagger, a_\beta^\dagger\} = 0$$

- "Easy" to demonstrate
- Rewrite antisymmetric state

$$\begin{aligned} |\alpha_1\alpha_2\alpha_3...\alpha_N\rangle &= a_{\alpha_1}^\dagger |\alpha_2\alpha_3...\alpha_N\rangle = a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger |\alpha_3...\alpha_N\rangle = ... \\ &= a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger ... a_{\alpha_N}^\dagger |0\rangle = \prod_i a_{\alpha_i}^\dagger |0\rangle \end{aligned}$$

- Ensures Pauli principle

$$\begin{aligned} |\alpha_1\alpha_2...\alpha_N\rangle &= a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger ... a_{\alpha_N}^\dagger |0\rangle = -a_{\alpha_2}^\dagger a_{\alpha_1}^\dagger ... a_{\alpha_N}^\dagger |0\rangle \\ &= -|\alpha_2\alpha_1...\alpha_N\rangle \end{aligned}$$

- Occupation numbers

$$|n_{\alpha_1} = 1, n_{\alpha_2} = 0, n_{\alpha_3} = 1, 0, ..., 0, ...\rangle = |\alpha_1\alpha_3\rangle$$

One-body operators in Fock space

- Examples?

- 1 particle in sp space $F = \sum_\alpha \sum_\beta |\alpha\rangle \langle\alpha| F |\beta\rangle \langle\beta|$

- Operator completely determined by all $\langle\alpha| F |\beta\rangle$ matrix elements

- N-particle space $F_N = F(1) + F(2) + ... + F(N) = \sum_{i=1}^{N} F(i)$
- Action of $F(i)$ on a product state

$$F(i)|\alpha_1\alpha_2\alpha_3...\alpha_N) = |\alpha_1\rangle |\alpha_2\rangle ... |\alpha_{i-1}\rangle \left\{ \sum_{\beta_i} |\beta_i\rangle \langle\beta_i| F |\alpha_i\rangle \right\} |\alpha_{i+1}\rangle ... |\alpha_N\rangle$$

$$= \sum_{\beta_i} \langle\beta_i| F |\alpha_i\rangle |\alpha_1...\alpha_{i-1}\beta_i\alpha_{i+1}...\alpha_N)$$

One-body operators (continued)

- Matrix element $\langle\beta_i| F |\alpha_i\rangle$ same for any particle (dummy variables)
- Then

$$F_N|\alpha_1\alpha_2\alpha_3...\alpha_N) = F(1)\,|\alpha_1\rangle\,|\alpha_2\rangle\,...\,|\alpha_N\rangle + ... + |\alpha_1\rangle\,|\alpha_2\rangle\,...F(N)\,|\alpha_N\rangle$$
$$= \sum_{\beta_1}\langle\beta_1| F |\alpha_1\rangle\,|\beta_1\alpha_2...\alpha_N) + ... + \sum_{\beta_N}\langle\beta_N| F |\alpha_N\rangle\,|\alpha_1\alpha_2...\beta_N)$$
$$= \sum_{i=1}^{N}\sum_{\beta_i}\langle\beta_i| F |\alpha_i\rangle\,|\alpha_1\alpha_2...\alpha_{i-1}\beta_i\alpha_{i+1}...\alpha_N)$$

- Since F_N is symmetric it commutes with the antisymmetrizer $\mathcal{A}$
- Thus

$$F_N\,|\alpha_1\alpha_2\alpha_3...\alpha_N\rangle = \sum_{i=1}^{N}\sum_{\beta_i}\langle\beta_i| F |\alpha_i\rangle\,|\alpha_1\alpha_2...\alpha_{i-1}\beta_i\alpha_{i+1}...\alpha_N\rangle$$

Fock-space one-body operator

- Consider Fock-space operator $$\hat{F} = \sum_{\alpha\beta} \langle\alpha| F |\beta\rangle \, a_\alpha^\dagger a_\beta$$
- Note the "^" notation
- This operator accomplishes the same as F_N for any N!
- Use

$$
\begin{aligned}
[\hat{F}, a_{\alpha_i}^\dagger] &= \sum_{\alpha\beta} \langle\alpha| F |\beta\rangle \, [a_\alpha^\dagger a_\beta, a_{\alpha_i}^\dagger] = \sum_{\alpha\beta} \langle\alpha| F |\beta\rangle \, (a_\alpha^\dagger a_\beta a_{\alpha_i}^\dagger - a_{\alpha_i}^\dagger a_\alpha^\dagger a_\beta) \\
&= \sum_{\alpha\beta} \langle\alpha| F |\beta\rangle \, a_\alpha^\dagger (a_\beta a_{\alpha_i}^\dagger + a_{\alpha_i}^\dagger a_\beta) = \sum_{\alpha\beta} \langle\alpha| F |\beta\rangle \, a_\alpha^\dagger \delta_{\beta,\alpha_i} \\
&= \sum_{\alpha} \langle\alpha| F |\alpha_i\rangle \, a_\alpha^\dagger = \sum_{\beta_i} \langle\beta_i| F |\alpha_i\rangle \, a_{\beta_i}^\dagger
\end{aligned}
$$

- and apply $\hat{F} \, |\alpha_1\alpha_2\alpha_3...\alpha_N\rangle = \hat{F} a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger ... a_{\alpha_N}^\dagger \, |0\rangle$

$$
\begin{aligned}
&= [\hat{F}, a_{\alpha_1}^\dagger] a_{\alpha_2}^\dagger ... a_{\alpha_N}^\dagger \, |0\rangle + a_{\alpha_1}^\dagger \hat{F} a_{\alpha_2}^\dagger ... a_{\alpha_N}^\dagger \, |0\rangle \\
&= [\hat{F}, a_{\alpha_1}^\dagger] a_{\alpha_2}^\dagger ... a_{\alpha_N}^\dagger \, |0\rangle + a_{\alpha_1}^\dagger [\hat{F}, a_{\alpha_2}^\dagger] ... a_{\alpha_N}^\dagger \, |0\rangle + ... + a_{\alpha_1}^\dagger a_{\alpha_2}^\dagger ... [\hat{F}, a_{\alpha_N}^\dagger] \, |0\rangle \\
&= \sum_{i=1}^{N} \sum_{\beta_i} \langle\beta_i| F |\alpha_i\rangle \, a_{\alpha_1}^\dagger ... a_{\alpha_{i-1}}^\dagger a_{\beta_i}^\dagger a_{\alpha_{i+1}}^\dagger ... a_{\alpha_N}^\dagger \, |0\rangle \\
&= \sum_{i=1}^{N} \sum_{\beta_i} \langle\beta_i| F |\alpha_i\rangle \, |\alpha_1 ... \alpha_{i-1} \beta_i \alpha_{i+1} ... \alpha_N\rangle \quad ✓
\end{aligned}
$$

Examples

- Density operator for N particles $\rho_N(\boldsymbol{r}) = \sum_{i=1}^{N} \delta(\boldsymbol{r} - \boldsymbol{r}_i)$

- Second-quantized form: choose $\{|\boldsymbol{r}, m_s\rangle\}$ basis
- In Fock space

$$\hat{\rho}(\boldsymbol{r}) = \sum_{m_s, m_{s'}} \int d^3r_1 \int d^3r'_1 \; \langle \boldsymbol{r}_1 m_s | \, \delta(\boldsymbol{r} - \boldsymbol{r}_{op}) \, | \boldsymbol{r}'_1 m_{s'} \rangle \; a^\dagger_{\boldsymbol{r}_1 m_s} a_{\boldsymbol{r}'_1 m_{s'}}$$

$$= \sum_{m_s} a^\dagger_{\boldsymbol{r} m_s} a_{\boldsymbol{r} m_s}$$

- Kinetic energy $\hat{T} = \sum_{\alpha\beta} \langle \alpha | \, T \, | \beta \rangle \, a^\dagger_\alpha a_\beta$

$$= \sum_{\boldsymbol{p}_1 m_1 \boldsymbol{p}_2 m_2} \langle \boldsymbol{p}_1 m_1 | \, \frac{\boldsymbol{p}^2_{op}}{2m} \, | \boldsymbol{p}_2 m_2 \rangle \; a^\dagger_{\boldsymbol{p}_1 m_1} a_{\boldsymbol{p}_2 m_2}$$

$$= \sum_{\boldsymbol{p}_1 m_1} \frac{\boldsymbol{p}^2_1}{2m} a^\dagger_{\boldsymbol{p}_1 m_1} a_{\boldsymbol{p}_1 m_1}$$

More examples

- Consider $\hat{N} = \sum_\alpha a^\dagger_\alpha a_\alpha$

- Determine $\left[\hat{N}, a^\dagger_{\alpha_i}\right]$
$$\begin{aligned} \left[\hat{N}, a^\dagger_{\alpha_i}\right] &= \sum_\alpha \left[a^\dagger_\alpha a_\alpha, a^\dagger_{\alpha_i}\right] \\ &= a^\dagger_{\alpha_i} \end{aligned}$$

- Therefore $\hat{N}\,|\alpha_1 ... \alpha_N\rangle = N\,|\alpha_1 ... \alpha_N\rangle$

Change of basis $\quad a^\dagger_\alpha\,|0\rangle = |\alpha\rangle = \sum_\lambda |\lambda\rangle\,\langle\lambda|\alpha\rangle = \sum_\lambda a^\dagger_\lambda\,|0\rangle\,\langle\lambda|\alpha\rangle$

Can be done for any state in Fock space ⇒ $\quad a^\dagger_\alpha = \sum_\lambda \langle\lambda|\alpha\rangle a^\dagger_\lambda$

Also $\quad a_\alpha = \sum_\lambda \langle\alpha|\lambda\rangle a_\lambda$

Two-body operators in Fock space

- Similar strategy $$V = \sum_{\alpha\beta}\sum_{\gamma\delta} |\alpha\beta)(\alpha\beta|V|\gamma\delta)(\gamma\delta|$$
- N-particles

$$V_N = \left\{ \begin{array}{ccccc} V(1,2)+ & V(1,3)+ & V(1,4)+ & \ldots + & V(1,N)+ \\ & V(2,3)+ & V(2,4)+ & \ldots + & V(2,N)+ \\ & & V(3,4)+ & \ldots + & V(3,N)+ \\ & & & \ddots & \vdots \\ & & & & V(N-1,N) \end{array} \right.$$

$$= \sum_{i<j=1}^{N} V(i,j) = \frac{1}{2}\sum_{i\neq j}^{N} V(i,j)$$

- Consider

$$V(i,j)|\alpha_1..\alpha_i..\alpha_j..\alpha_N) = \sum_{\beta_i\beta_j} (\beta_i\beta_j|V|\alpha_i\alpha_j)|\alpha_1..\alpha_{i-1}\beta_i\alpha_{i+1}..\alpha_{j-1}\beta_j\alpha_{j+1}..\alpha_N)$$

- Matrix elements do not depend on the selected pair
- $(\beta_i\beta_j|V|\alpha_i\alpha_j)$ identical for any pair as long as quantum numbers are the same, so

$$V_N|\alpha_1\alpha_2\alpha_3...\alpha_N) = \sum_{i<j=1}^{N}\sum_{\beta_i\beta_j} (\beta_i\beta_j|V|\alpha_i\alpha_j)|\alpha_1...\beta_i...\beta_j...\alpha_N)$$

More on two-body operators

- Note: V_N symmetric and therefore commutes with antisymmetrizer
- As a consequence

$$V_N \left|\alpha_1 \alpha_2 \alpha_3 ... \alpha_N\right\rangle = \sum_{i<j=1}^{N} \sum_{\beta_i \beta_j} (\beta_i \beta_j | V | \alpha_i \alpha_j) \left|\alpha_1 ... \beta_i ... \beta_j ... \alpha_N\right\rangle$$

- Fock-space operator

$$\hat{V} = \frac{1}{2} \sum_{\alpha\beta\gamma\delta} (\alpha\beta|V|\gamma\delta) a_\alpha^\dagger a_\beta^\dagger a_\delta a_\gamma$$

- accomplishes the same result for any particle number!
- Note ordering

Two-body operator

- Use

$$
\begin{aligned}
[\hat{V}, a^\dagger_{\alpha_i}] &= \frac{1}{2}\sum_{\alpha\beta\gamma\delta}(\alpha\beta|V|\gamma\delta)a^\dagger_\alpha a^\dagger_\beta [a_\delta a_\gamma, a^\dagger_{\alpha_i}] \\
&= \ldots\ldots a^\dagger_\alpha a^\dagger_\beta (a_\delta a_\gamma a^\dagger_{\alpha_i} - a^\dagger_{\alpha_i} a_\delta a_\gamma) \\
&= \ldots\ldots a^\dagger_\alpha a^\dagger_\beta (a_\delta(\delta_{\gamma,\alpha_i} - a^\dagger_{\alpha_i} a_\gamma) - a^\dagger_{\alpha_i} a_\delta a_\gamma) \\
&= \ldots\ldots a^\dagger_\alpha a^\dagger_\beta (a_\delta \delta_{\gamma,\alpha_i} - \delta_{\delta,\alpha_i} a_\gamma) \\
&= \frac{1}{2}\sum_{\alpha\beta\delta}(\alpha\beta|V|\alpha_i\delta)a^\dagger_\alpha a^\dagger_\beta a_\delta - \frac{1}{2}\sum_{\alpha\beta\gamma}(\alpha\beta|V|\gamma\alpha_i)a^\dagger_\alpha a^\dagger_\beta a_\gamma \\
&= \sum_{\alpha\beta\delta}(\alpha\beta|V|\alpha_i\delta)a^\dagger_\alpha a^\dagger_\beta a_\delta = \sum_{\beta_i\beta_j\alpha_{i'}}(\beta_i\beta_j|V|\alpha_i\alpha_{i'})a^\dagger_{\beta_i} a^\dagger_{\beta_j} a_{\alpha_{i'}}
\end{aligned}
$$

- Note $(\alpha\beta|V|\gamma\delta) = (\beta\alpha|V|\delta\gamma)$ since $V(i,j) = V(j,i)$

Two-body operators

- Use to show

$$\hat{V}\,|\alpha_1\alpha_2\alpha_3...\alpha_N\rangle = \hat{V} a^\dagger_{\alpha_1} a^\dagger_{\alpha_2}...a^\dagger_{\alpha_N}\,|0\rangle$$
$$= \sum_{i=1}^{N} a^\dagger_{\alpha_1}...[\hat{V}, a^\dagger_{\alpha_i}]...a^\dagger_{\alpha_N}\,|0\rangle$$
$$= \sum_{i=1}^{N} \sum_{\beta_i\beta_{i'}\alpha_{i'}} (\beta_i\beta_{i'}|V|\alpha_i\alpha_{i'}) a^\dagger_{\alpha_1}...a^\dagger_{\beta_i} a^\dagger_{\beta_{i'}} a_{\alpha_{i'}} a^\dagger_{\alpha_{i+1}}...a^\dagger_{\alpha_N}\,|0\rangle$$
$$= \sum_{i=1}^{N}\sum_{j>i}^{N}\sum_{\beta_i\beta_j} (\beta_i\beta_j|V|\alpha_i\alpha_j) a^\dagger_{\alpha_1}...a^\dagger_{\beta_i}...a^\dagger_{\beta_j}...a^\dagger_{\alpha_N}\,|0\rangle \quad ✓$$

- Employ

$$\sum_{\beta_j\alpha_{i'}} f(\beta_j,\alpha_{i'})[a^\dagger_{\beta_j} a_{\alpha_{i'}}, a^\dagger_{\alpha_j}] = \sum_{\beta_j} f(\beta_j,\alpha_j) a^\dagger_{\beta_j}$$

- Often used

$$\hat{V} = \frac{1}{4}\sum_{\alpha\beta\gamma\delta} \langle\alpha\beta|\,V\,|\gamma\delta\rangle\, a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma$$

- with

$$\langle\alpha\beta|\,V\,|\gamma\delta\rangle \equiv (\alpha\beta|V|\gamma\delta) - (\alpha\beta|V|\delta\gamma) = \langle\alpha\beta|\,\hat{V}\,|\gamma\delta\rangle$$

- Check!

Hamiltonian

- Most common operator $$\hat{H} = \hat{T} + \hat{V} = \sum_{\alpha\beta} \langle\alpha|\, T \,|\beta\rangle\, a^\dagger_\alpha a_\beta + \frac{1}{2}\sum_{\alpha\beta\gamma\delta} (\alpha\beta|V|\gamma\delta) a^\dagger_\alpha a^\dagger_\beta a_\delta a_\gamma$$
- Notation often used $\psi^\dagger_{m_s}(\boldsymbol{r}) \equiv a^\dagger_{\boldsymbol{r}m_s}$
- Use
$$\begin{aligned} \langle \boldsymbol{r} m_s|\, T \,|\boldsymbol{r}' m_s'\rangle &= \langle \boldsymbol{r} m_s|\, \frac{\boldsymbol{p}^2}{2m} \,|\boldsymbol{r}' m_s'\rangle \\ &= \frac{-i\hbar}{2m} \nabla \cdot \langle\, \boldsymbol{r} m_s|\, \boldsymbol{p} \,|\boldsymbol{r}' m_s'\rangle \\ &= \frac{-\hbar^2}{2m} \nabla^2 \langle \boldsymbol{r} m_s|\boldsymbol{r}' m_s'\rangle \\ &= \frac{-\hbar^2}{2m} \nabla^2 \delta(\boldsymbol{r} - \boldsymbol{r}')\delta_{m_s,m_s'} \end{aligned}$$
- and
$$\begin{aligned} (\boldsymbol{r}_1 m_{s_1}\ \boldsymbol{r}_2 m_{s_2}|V(\boldsymbol{r},\boldsymbol{r}')|\boldsymbol{r}_3 m_{s_3}\ \boldsymbol{r}_4 m_{s_4}) &= \delta(\boldsymbol{r}_1 - \boldsymbol{r}_3)\delta(\boldsymbol{r}_2 - \boldsymbol{r}_4) \\ &\times\ \delta_{m_{s_1},m_{s_3}}\delta_{m_{s_2},m_{s_4}} V(|\boldsymbol{r}_3 - \boldsymbol{r}_4|) \end{aligned}$$
- In this basis
$$\begin{aligned} \hat{H} &= \sum_{m_s} \int d^3r\ \psi^\dagger_{m_s}(\boldsymbol{r})\{\frac{-\hbar^2}{2m}\nabla^2\}\psi_{m_s}(\boldsymbol{r}) \\ &+\ \frac{1}{2}\sum_{m_s m_s'} \int d^3r \int d^3r'\ \psi^\dagger_{m_s}(\boldsymbol{r})\psi^\dagger_{m_s'}(\boldsymbol{r}')V(|\boldsymbol{r} - \boldsymbol{r}'|)\psi_{m_s'}(\boldsymbol{r}')\psi_{m_s}(\boldsymbol{r}) \end{aligned}$$
- appears as “second quantization”