S04E01 Second quantization

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1 The many-particle Hilbert space

$$\mathcal{F} = \mathcal{H}^0 \oplus \mathcal{H}^1 \oplus \mathcal{H}^2 \oplus \mathcal{H}^3 \oplus \cdots$$

We have

$$\begin{aligned}\Psi &= \Psi^0 + \Psi^1 + \Psi^2 + \Psi^3 + \cdots \\ &= \Psi^0 + C_i|\psi_i\rangle + C_{ij}|\psi_i\rangle|\psi_j\rangle + C_{ijk}|\psi_i\rangle|\psi_j\rangle|\psi_k\rangle + \cdots\end{aligned}$$

and

$$\begin{aligned}\mathcal{P}_{12}C_{ij\dots}|\psi_i\rangle|\psi_j\rangle\cdots &= C_{ij\dots}|\psi_j\rangle|\psi_i\rangle\cdots \\ &= C_{ji\dots}|\psi_i\rangle|\psi_j\rangle\cdots\end{aligned}$$

which means that

$$C_{ji\dots} = \zeta C_{ij\dots}$$

Therefore, we define

$$|\psi_i\psi_j\cdots\rangle = \frac{1}{\sqrt{n!}}\sum_{\mathcal{P}}\zeta_{\mathcal{P}}|\psi_{\mathcal{P}i}\rangle|\psi_{\mathcal{P}j}\rangle\cdots$$

which is an over-complete basis of the n-particle Hilbert space

$$\begin{aligned}\langle\phi_i\phi_j\cdots|\psi_k\psi_l\cdots\rangle &= \frac{1}{n!}\sum_{\mathcal{P}}\sum_{\mathcal{Q}}\zeta_{\mathcal{P}}\zeta_{\mathcal{Q}}\langle\phi_{\mathcal{P}i}|\psi_{\mathcal{Q}k}\rangle\langle\phi_{\mathcal{P}j}|\psi_{\mathcal{Q}l}\rangle\cdots \\ &= \sum_{\mathcal{R}}\zeta_{\mathcal{R}}\langle\phi_i|\psi_{\mathcal{R}k}\rangle\langle\phi_j|\psi_{\mathcal{R}l}\rangle\cdots \qquad \mathcal{Q}=\mathcal{R}\mathcal{P} \\ &= \det\begin{pmatrix}\langle\phi_i|\psi_k\rangle & \langle\phi_i|\psi_l\rangle & \cdots \\ \langle\phi_j|\psi_k\rangle & \langle\phi_j|\psi_l\rangle & \cdots \\ \vdots & \vdots & \ddots\end{pmatrix}\end{aligned}$$

In particular, we have

$$\langle \psi_i \psi_i \cdots \psi_i \psi_j \psi_j \cdots \psi_j \cdots | \psi_i \psi_i \cdots \psi_i \psi_j \psi_j \cdots \psi_j \cdots \rangle = n_i! n_j! \cdots$$

A natural complete orthonormal basis of the n-particle subspace $\mathcal{H}^n$ is the occupation number basis

$$|n_i n_j \cdots \rangle = \frac{|\psi_i \psi_i \cdots \psi_i \psi_j \psi_j \cdots \psi_j \cdots \rangle}{\sqrt{n_i! n_j! \cdots}}$$

2 Creation and annihilation operators

We define

$$a^\dagger(\psi) |\psi_i \psi_j \cdots \rangle \equiv |\psi \psi_i \psi_j \cdots \rangle$$

such that using

$$\begin{aligned} \langle \phi_i \phi_j \cdots | a(\psi) | \psi_k \psi_l \cdots \rangle &= \langle \psi_k \psi_l \cdots | a^\dagger(\psi) | \phi_i \phi_j \cdots \rangle^* \\ &= \langle \psi_k \psi_l \cdots | \psi \phi_i \phi_j \cdots \rangle^* \\ &= \langle \psi \phi_i \phi_j \cdots | \psi_k \psi_l \cdots \rangle \end{aligned}$$

one can prove that

$$a^\dagger(\phi)\, a^\dagger(\psi) - \zeta\, a^\dagger(\psi)\, a^\dagger(\phi) = 0$$

and its conjugate, as well as

$$a(\phi)\, a^\dagger(\psi) - \zeta\, a(\psi)\, a^\dagger(\phi) = \langle \phi | \psi \rangle$$

3 Second quantized operators

In the Fock space, n-body operators $\widetilde{\mathcal{O}}_n$ lifted from $\mathcal{O}_n : \mathcal{H}^n \to \mathcal{H}^n$ take the form

$$\widetilde{\mathcal{O}}_n = \widetilde{\mathcal{O}}_n|_{\mathcal{H}0} \oplus \widetilde{\mathcal{O}}_n|_{\mathcal{H}1} \oplus \widetilde{\mathcal{O}}_n|_{\mathcal{H}2} \oplus \widetilde{\mathcal{O}}_n|_{\mathcal{H}3} \oplus \cdots$$

3.1 One-body operators

are familiar: their restrictions are like the total angular momentum operator of n particles, namely

$$\widetilde{\mathcal{O}}_1|_{\mathcal{H}n} = \left(\mathcal{O}_1 \otimes 1 \otimes \cdots \otimes 1\right) + \left(1 \otimes \mathcal{O}_1 \otimes \cdots \otimes 1\right) + \cdots + \left(1 \otimes 1 \otimes \cdots \otimes \mathcal{O}_1\right)$$

It is then easy to verify that

$$\begin{aligned}\widetilde{\mathcal{O}}_1 &= \mathcal{O}_{1i}\, a^\dagger(\psi_i)\, a(\psi_i) \\ &= \mathcal{O}_{1i}\, \langle\phi_j|\psi_i\rangle\langle\psi_i|\phi_k\rangle\, a^\dagger(\phi_j)\, a(\phi_k) \\ &= \langle\phi_j|\mathcal{O}_1|\phi_k\rangle\, a^\dagger(\phi_j)\, a(\phi_k)\end{aligned}$$

since the lifted one-body operator is invariant (symmetric) under permutations.

3.2 Two-body operators

Notice that we may always write

$$\mathcal{O}_2 = \sum_{I\le J} C_{IJ}\left[\left(\mathcal{O}_{1I}\otimes\mathcal{O}_{1J}\right)+\left(\mathcal{O}_{1J}\otimes\mathcal{O}_{1I}\right)\right]$$

since the original two-body operator is (always) symmetric under permutations.

For concreteness, take the three-particle Hilbert space as an example,

$$\begin{aligned}\widetilde{\mathcal{O}}_2|_{\mathcal{H}3} = C_{IJ}&\left[\left(\mathcal{O}_{1I}\otimes\mathcal{O}_{1J}\otimes 1\right)+\left(\mathcal{O}_{1I}\otimes 1\otimes\mathcal{O}_{1J}\right)+\left(1\otimes\mathcal{O}_{1I}\otimes\mathcal{O}_{1J}\right)\right] \\ &+ C_{IJ}\left[\left(\mathcal{O}_{1J}\otimes\mathcal{O}_{1I}\otimes 1\right)+\left(\mathcal{O}_{1J}\otimes 1\otimes\mathcal{O}_{1I}\right)+\left(1\otimes\mathcal{O}_{1J}\otimes\mathcal{O}_{1I}\right)\right]\end{aligned}$$

where we have suppressed the $\sum_{I\le J}$ symbol. Notice that this can be written as

$$\widetilde{\mathcal{O}}_2|_{\mathcal{H}3} = C_{IJ}\,\widetilde{\mathcal{O}}_{1I}|_{\mathcal{H}3}\widetilde{\mathcal{O}}_{1J}|_{\mathcal{H}3} - C_{IJ}\,\widetilde{\mathcal{O}}_{1I}\widetilde{\mathcal{O}}_{1J}|_{\mathcal{H}3}$$

where

$$\widetilde{\mathcal{O}}_{1I}\widetilde{\mathcal{O}}_{1J}|_{\mathcal{H}3} = \left(\mathcal{O}_{1I}\mathcal{O}_{1J}\otimes 1\otimes 1\right)+\left(1\otimes\mathcal{O}_{1I}\mathcal{O}_{1J}\otimes 1\right)+\left(1\otimes 1\otimes\mathcal{O}_{1I}\mathcal{O}_{1J}\right)$$

The two-body operator can now be written as

$$\begin{aligned}\widetilde{\mathcal{O}}_2 &= C_{IJ}\,\langle\phi_i|\mathcal{O}_{1I}|\phi_j\rangle\langle\phi_k|\mathcal{O}_{1J}|\phi_l\rangle\, a^\dagger(\phi_i)\, a(\phi_j)\, a^\dagger(\phi_k)\, a(\phi_l) \\ &\qquad - C_{IJ}\,\langle\phi_i|\mathcal{O}_{1I}\mathcal{O}_{1J}|\phi_l\rangle\, a^\dagger(\phi_i)\, a(\phi_l) \\ &= C_{IJ}\,\langle\phi_i|\mathcal{O}_{1I}|\phi_j\rangle\langle\phi_k|\mathcal{O}_{1J}|\phi_l\rangle\, a^\dagger(\phi_i)\, a(\phi_j)\, a^\dagger(\phi_k)\, a(\phi_l) \\ &\qquad - C_{IJ}\,\langle\phi_i|\mathcal{O}_{1I}|\phi_j\rangle\langle\phi_k|\mathcal{O}_{1J}|\phi_l\rangle\, a^\dagger(\phi_i)\, a(\phi_l)\,\delta_{jk} \\ &= C_{IJ}\,\langle\phi_i|\mathcal{O}_{1I}|\phi_j\rangle\langle\phi_k|\mathcal{O}_{1J}|\phi_l\rangle\, a^\dagger(\phi_i)\, a^\dagger(\phi_k)\, a(\phi_l)\, a(\phi_j) \qquad \text{or} \\ &= C_{IJ}\,\langle\phi_k|\mathcal{O}_{1J}|\phi_l\rangle\langle\phi_i|\mathcal{O}_{1I}|\phi_j\rangle\, a^\dagger(\phi_k)\, a^\dagger(\phi_i)\, a(\phi_j)\, a(\phi_l) \qquad \text{as well}\end{aligned}$$

and we finally conclude that

$$\widetilde{\mathcal{O}}_2 = \tfrac{1}{2}\sum\langle\phi_i|\langle\phi_k|\mathcal{O}_2|\phi_j\rangle|\phi_l\rangle\, a^\dagger(\phi_i)\, a^\dagger(\phi_k)\, a(\phi_l)\, a(\phi_j)$$

4 The number operator

is the identity operator $1 : \mathcal{H}^1 \to \mathcal{H}^1$ lifted to the Fock space: $\mathcal{N} = a^\dagger(\phi_i)\, a(\phi_i)$.

5 Quantum statistical mechanics

is governed by

$$\rho = Z^{-1} e^{-\beta\mathcal{H}+\beta\mu\mathcal{N}}$$

6 The Hartree-Fock approximation

The Hamiltonian is

$$H = \sum \langle\phi_i|\mathcal{O}_1|\phi_j\rangle\, a^\dagger(\phi_i)\, a(\phi_j) + \tfrac{1}{2}\sum \langle\phi_i|\langle\phi_k|\mathcal{O}_2|\phi_j\rangle|\phi_l\rangle\, a^\dagger(\phi_i)\, a^\dagger(\phi_k)\, a(\phi_l)\, a(\phi_j)$$

and the Hartree-Fock variational ground state is a Fermi sea:

$$|\Omega\rangle = \prod_{\text{occ.}} a^\dagger(\phi_i)|\text{vac.}\rangle$$

Therefore, the expectation value of the ground state energy is

$$\langle\Omega|H|\Omega\rangle = \sum_{\text{occ.}} \langle\phi_i|\mathcal{O}_1|\phi_i\rangle + \tfrac{1}{2}\sum_{\text{occ.}} \langle\phi_i|\langle\phi_k|\mathcal{O}_2|\phi_i\rangle|\phi_k\rangle - \tfrac{1}{2}\sum_{\text{occ.}} \langle\phi_i|\langle\phi_k|\mathcal{O}_2|\phi_k\rangle|\phi_i\rangle$$

If we vary the states ϕ_i under the normalization constraint

$$\langle\phi_i|\phi_i\rangle = 1$$

we obtain the Hartree-Fock equation

$$\begin{aligned}
\varepsilon_i|\phi_i\rangle &= \sum_{\text{occ.}} \mathcal{O}_1|\phi_i\rangle + \tfrac{1}{2}\sum_{\text{occ.}} \langle\cdot|\langle\phi_k|\mathcal{O}_2|\phi_i\rangle|\phi_k\rangle + \tfrac{1}{2}\sum_{\text{occ.}} \langle\phi_k|\langle\cdot|\mathcal{O}_2|\phi_k\rangle|\phi_i\rangle \\
&\qquad - \tfrac{1}{2}\sum_{\text{occ.}} \langle\cdot|\langle\phi_k|\mathcal{O}_2|\phi_k\rangle|\phi_i\rangle - \tfrac{1}{2}\sum_{\text{occ.}} \langle\phi_k|\langle\cdot|\mathcal{O}_2|\phi_i\rangle|\phi_k\rangle \qquad \text{simplify} \\
\varepsilon_i|\phi_i\rangle &= \sum_{\text{occ.}} \mathcal{O}_1|\phi_i\rangle + \sum_{\text{occ.}} \langle\cdot|\langle\phi_k|\mathcal{O}_2|\phi_i\rangle|\phi_k\rangle - \sum_{\text{occ.}} \langle\cdot|\langle\phi_k|\mathcal{O}_2|\phi_k\rangle|\phi_i\rangle
\end{aligned}$$

since the two-body operator is symmetric under permutations.