15.4: Multiple Particles and Second Quantization

In the case of a large number of nuclear or electronic degrees of freedom (or for photons in a quantum light field), it becomes tedious to write out the explicit product-state form of the state vector, i.e.,

$$|\psi\rangle = |\varphi_1, \varphi_2, \varphi_3 \cdots\rangle \tag{15.4.1}$$

Under these circumstances it becomes useful to define creation and annihilation operators. If $|\psi\rangle$ refers to the state of multiple harmonic oscillators, then the Hamiltonian has the form

$$H = \sum_\alpha \left(\frac{p_\alpha^2}{2m_\alpha} + \frac{1}{2} m_\alpha \omega_\alpha^2 q_\alpha^2 \right) \tag{15.4.2}$$

which can also be expressed as

$$H = \sum_\alpha \hbar\omega_\alpha \left(a_\alpha^\dagger a_\alpha + \frac{1}{2} \right) \tag{15.4.3}$$

and the eigenstates represented in through the occupation of each oscillator

$$|\psi\rangle = |n_1, n_2, n_3 \ldots). \tag{15.4.4}$$

This representation is sometimes referred to as “second quantization”, because the classical Hamiltonian was initially quantized by replacing the position and momentum variables by operators, and then these quantum operators were again replaced by raising and lowering operators.

The operator $a_\alpha^\dagger$ raises the occupation in mode $|n_\alpha\rangle$, and a_α lowers the excitation in mode $|n_\alpha\rangle$. The eigenvalues of these operators, $n_\alpha \rightarrow n_\alpha \pm 1$, are captured by the commutator relationships:

$$\left[a_\alpha, a_\beta^\dagger\right] = \delta_{\alpha\beta} \tag{15.4.5}$$

$$[a_\alpha, a_\beta] = 0 \tag{15.4.6}$$

Equation 15.4.5 indicates that the raising and lower operators do not commute if they are operators in the same degree of freedom ($\alpha = \beta$), but they do otherwise. Written another way, these expression indicate that the order of operations for the raising and lowering operators in different degrees of freedom commute.

$$a_\alpha a_\beta^\dagger = a_\beta^\dagger a_\alpha \tag{15.4.7}$$

$$a_\alpha a_\beta = a_\beta a_\alpha] \tag{15.4.8}$$

$$a_\alpha^\dagger a_\beta^\dagger = a_\beta^\dagger a_\alpha^\dagger \tag{15.4.9}$$

These expressions also imply that the eigenfunctions operations of the forms in Equations 15.4.7-15.4.9 are the same, so that these eigenfunctions should be symmetric to interchange of the coordinates. That is, these particles are bosons.

This observations proves an avenue to defining raising and lowering operators for electrons. Electrons are fermions, and therefore *antisymmetric* to exchange of particles. This suggests that electrons will have raising and lowering operators that change the excitation of an electronic state up or down following the relationship

$$b_\alpha b_\beta^\dagger = -b_\beta^\dagger b_\alpha \tag{15.4.10}$$

or

$$\left[b_\alpha, b_\beta^\dagger\right]_+ = \delta_{\alpha\beta} \tag{15.4.11}$$

where $[\ldots]_+$ refers to the *anti-commutator*. Further, we write

$$[b_\alpha, b_\beta]_+ = 0 \tag{15.4.12}$$

This comes from considering the action of these operators for the case where $\alpha = \beta$. In that case, taking the Hermetian conjugate, we see that Equation 15.4.12gives

$$2b_\alpha^\dagger b_\alpha^\dagger = 0 \tag{15.4.13}$$

or

$$b_\alpha^\dagger b_\alpha^\dagger = 0 \tag{15.4.14}$$

This relationship says that we cannot put two excitations into the same state, as expected for Fermions. This relationship indicates that there are only two eigenfunctions for the operators $b_\alpha^\dagger$ and b_α, namely $|n_\alpha = 0\rangle$ and $|n_\alpha = 1\rangle$. This is also seen with Equation 15.4.11, which indicates that

$$b_\alpha^\dagger b_\alpha |n_\alpha\rangle + b_\alpha b_\alpha^\dagger |n_\alpha\rangle = |n_\alpha\rangle \tag{15.4.15}$$

or

$$b_\alpha b_\alpha^\dagger |n_\alpha\rangle = \left(1 - b_\alpha^\dagger b_\alpha\right) |n_\alpha\rangle \tag{15.4.16}$$

If we now set $|n_\alpha\rangle = |0\rangle$, we find that Equation 15.4.16implies

$$\begin{aligned} b_\alpha b_\alpha^\dagger |0\rangle &= |0\rangle \\ b_\alpha^\dagger b_\alpha |0\rangle &= 0 \\ b_\alpha b_\alpha^\dagger |1\rangle &= 0 \\ b_\alpha^\dagger b_\alpha |1\rangle &= |1\rangle \end{aligned} \tag{15.4.17}$$

Again, this reinforces that only two states, $|0\rangle$ and $|1\rangle$, are allowed for electron raising and lowering operators. These are known as Pauli operators, since they implicitly enforce the Pauli exclusion principle. Note, in Equation 15.4.17, that $|0\rangle$ refers to the eigenvector with an eigenvalue of zero $|\varphi_0\rangle$, whereas "0" refers to the null vector.

Frenkel Excitons

For electronic chromophores, we use the notation $|g\rangle$ and $|e\rangle$ for the states of an electron in its ground or excited state. The state of the system for one excitation in an aggregate

$$|n\rangle = |g, g, g, g \ldots e \ldots g\rangle \tag{15.4.18}$$

can then be written as $a_n^\dagger |G\rangle$, or simply $a_n^\dagger$, and the Frenkel exciton Hamiltonian is

$$H_0 = \sum_{n=0}^{N-1} \varepsilon_0 |n\rangle\langle n| + \sum_{n,m} J_{n,m} |n\rangle\langle m| \tag{15.4.19}$$

or

$$H_0 = \sum_n \varepsilon_0 b_n^\dagger b_n + \sum_{n,m} J_{n,m} b_n^\dagger b_m \tag{15.4.20}$$

Readings

1. Schatz, G. C.; Ratner, M. A., Quantum Mechanics in Chemistry. Dover Publications: Mineola, NY, 2002; p. 119.