

## 6 Advantages of Second Quantization—Illustrative Examples

### 6.1 General

Throughout the previous sections we become acquainted with the basic notations and rules of second quantization. It is time now to utilize the benefits of this formalism. In this section the usefulness of the second quantized approach will be illustrated from the practical point of view on a few selected simple examples. In fact, this formalism can only be appreciated by those who really use it in practice. It is hoped that the following development and examples will help the reader to appreciate the beauty and power of this formalism and to give him/her the possibility to apply it in his/her work. Before turning to the concrete examples, some general remarks are made in order to put the second quantized formalism to its proper place. Some of the following remarks have already been noted before, but it appears to be useful to collect here the most important points.

Advantages of second quantization are both conceptual and practical. The conceptual benefits concern the following features of the many-electron theory:

- (i) In the second quantized form of the Hamiltonian there is no explicit reference to the number of electrons of the system,  $N$ . This is an advantage in quantum field theory of systems with variable particle numbers, or in solid-state physics where one has an infinite number of electrons. In quantum chemistry, this feature is important, e.g., in studying ionization processes: the ion and the neutral molecule (or atom) can be described by one and the same Hamiltonian. The wave functions of ions and neutral systems can be considered as different states of the same Hamiltonian, provided that the same set of one-electron basis functions is used. This feature will be utilized, e.g., in Sect. 10.2 discussing particle-hole symmetry, and it also permits one to derive appropriate expressions for ionization potentials (Pickup & Goscinski 1973; Öhrn & Born 1981; Paul 1982; Oddershede 1987).
- (ii) The antisymmetry of the many-electron wave function is automatically ensured by second quantization due to the anticommutation properties of creation/annihilation operators.
- (iii) It is possible to introduce a partitioning of the total Hamiltonian by a classification of the one-electron basis orbitals, i.e., of the list of one- and two-electron integrals in a given basis set. Thus, the second quantized Hamiltonian is well suited for studying interacting subsystems. We shall utilize this property in Sects. 15–16.

- (iv) There are also some features of the many-electron problem which would be difficult to understand without second quantization. The inherent connection between the  $N$ -electron problem and the unitary group can be cited as an example (cf. Sect. 17.2).

Practical benefits of second quantization are consequences of the above conceptual advantages. For the forthcoming simple introduction, the above point (ii) is the most important one. This allows us to understand and derive many formulae and theorems of quantum chemistry in a very simple manner.

## 6.2 Overlap of Two Determinants

Matrix elements between determinantal wave functions can be evaluated by the so-called Slater (or Slater-Condon) rules. We shall not derive the Slater rules in general, but in some particular cases the first and second quantization-based derivations will be compared.

Consider the overlap:

$$S_{KL} = \langle \Phi_K | \Phi_L \rangle \quad (6.1)$$

where  $\Phi_K$  and  $\Phi_L$  are two determinants constructed by orthonormalized one-electron functions:

$$\Phi_K = |\phi_{K_1}, \phi_{K_2}, \dots, \phi_{K_N}| \quad (6.2a)$$

$$\Phi_L = |\phi_{L_1}, \phi_{L_2}, \dots, \phi_{L_N}|. \quad (6.2b)$$

Evaluation of  $S_{KL}$  in the framework of the “first quantized” procedure proceeds along the following lines. Substituting the determinants of Eq. (6.2) into Eq. (6.1), one writes:

$$S_{KL} = \left\langle \frac{1}{\sqrt{N!}} \sum_P (-1)^P \phi_{K_1}(P_1) \dots \phi_{K_N}(P_N) \middle| \frac{1}{\sqrt{N!}} \sum_Q (-1)^Q \phi_{L_1}(Q_1) \dots \phi_{L_N}(Q_N) \right\rangle. \quad (6.3)$$

An analysis of this expression makes clear that it should vanish if there is no perfect coincidence of the MOs in the *bra*- and the *ket*-functions. So the two determinants should be the same:

$$S_{KL} = S_{KK} \delta_{KL}. \quad (6.4)$$

The quantity  $S_{KK}$  can be evaluated as follows:

$$S_{KK} = \frac{1}{N!} \sum_{PQ} (-1)^{P+Q} \langle \hat{P} \phi_1(1) \dots \phi_N(N) | \hat{Q} \phi_1(1) \dots \phi_N(N) \rangle. \quad (6.5)$$

where  $\hat{P}$  and  $\hat{Q}$  denote the appropriate permutation operators. We can observe