Motivating second quantization

Note: In what follows, the terminology "n-electron function" will refer to an antisymmetric function of n space-spin coordinates $(i) \equiv (\mathbf{r}_i, s_i)$. We implicitly take every integral to be a definite integral over all values of $(\mathbf{r}_i, s_i)$.

Annihilation operators. Let $\{\psi_p\}$ be a complete basis of spin-orbitals and let $\Phi_{(p_1 \cdots p_n)}$ denote the n-electron Slater determinant formed from $\psi_{p_1}, \ldots, \psi_{p_n}$. Then it is possible to define an operator $\hat{a}_{p_1}$ which deletes ψ_{p_1} from $\Phi_{(p_1 \cdots p_n)}$ to produce $\Phi_{(p_2 \cdots p_n)}$, the $(n-1)$-electron Slater determinant formed from $\psi_{p_2}, \ldots, \psi_{p_n}$. We can define such an "annihilator" $\hat{a}_p$ of spin-orbital ψ_p explicitly as

$$(\hat{a}_p \Psi)(2, \ldots, m) \equiv \sqrt{m} \int d(1)\ \psi_p^*(1) \Psi(1, 2, \ldots, m) \tag{1}$$

which takes an m-electron function Ψ into the $(m-1)$-electron function $\hat{a}_p \Psi$. Applied to $\Phi_{(p_1 \cdots p_n)}$, this gives

$$\hat{a}_p \Phi_{(p_1 \cdots p_n)} = \begin{cases} (-)^{k-1} \Phi_{(p_1 \cdots \cancel{p_k} \cdots p_n)} & \text{if } p = p_k \in (p_1 \cdots p_n) \\ 0 & \text{otherwise.} \end{cases} \tag{2}$$

As an exercise, it is worth proving to yourself that the definition in equation 1 satisfies equation 2.

Annihilation operators anticommute. Consider the action of two annihilators $\hat{a}_p$ and $\hat{a}_q$ on an n-electron function Ψ. If $\hat{a}_p$ is applied first, we obtain

$$(\hat{a}_q \hat{a}_p \Psi)(3, \ldots, n) = \sqrt{n(n-1)} \int d(1) d(2)\ \psi_p^*(1) \psi_q^*(2) \Psi(1, 2, 3, \ldots, n)$$

whereas if $\hat{a}_q$ is applied first, we obtain

$$(\hat{a}_p \hat{a}_q \Psi)(3, \ldots, n) = \sqrt{n(n-1)} \int d(1) d(2)\ \psi_q^*(1) \psi_p^*(2) \Psi(1, 2, 3, \ldots, n)\ .$$

This last integral can be rewritten as

$$\int d(1) d(2)\ \psi_p^*(1) \psi_q^*(2) \Psi(2, 1, 3, \ldots, n) = -\int d(1) d(2)\ \psi_p^*(1) \psi_q^*(2) \Psi(1, 2, 3, \ldots, n)$$

by swapping dummy variables of integration $(1 \leftrightarrow 2)$ and using the antisymmetry of Ψ. This shows that $\hat{a}_p \hat{a}_q \Psi = -\hat{a}_q \hat{a}_p \Psi$ and, restricting ourselves to the space of m-electron $(m = 0, 1, 2, \ldots, \infty)$ functions, we have the identity

$$[\hat{a}_p, \hat{a}_q]_+ \equiv \hat{a}_p \hat{a}_q + \hat{a}_q \hat{a}_p = 0 \tag{3}$$

i.e. the annihilation operators anticommute. Note that restriction to antisymmetric functions is key – were we to restrict ourselves to *symmetric* functions, equation 1 would define operators which instead satisfy $\hat{a}_p \hat{a}_q - \hat{a}_q \hat{a}_p = 0$.

Ψ decomposition. Using these newfangled operators, any n-electron function can be decomposed as

$$\Psi(1, \cdots, n) = \frac{1}{\sqrt{n}} \sum_p^{\infty} \psi_p(1)\ (\hat{a}_p \Psi)(2, \ldots, n) = \frac{1}{\sqrt{n(n-1)}} \sum_{pq}^{\infty} \psi_p(1) \psi_q(2)\ (\hat{a}_q \hat{a}_p \Psi)(3, \ldots, n) \tag{4}$$

by resolution of the identity along one or two sets of electron coordinates (recall the definition in equation 1).[1]

[1] In principle, this could be carried on to eliminate all of the coordinates from Ψ. The scalars $(\hat{a}_{p_n} \cdots \hat{a}_{p_1} \Psi)$ in this expansion would then be equal to $\sqrt{n!}\ c_{p_1 \cdots p_n}$, where $c_{p_1 \cdots p_n}$ is the expansion coefficient of Ψ in the basis of spin-orbital products.

Expressing $\hat{H}_e$ in terms of annihilation operators. The electronic Hamiltonian[2] of an n-electron system can be written as

$$\hat{H}_e = \sum_i^n \hat{h}(i) + \sum_{i<j}^n \hat{g}(i,j) \qquad \hat{h}(i) = -\frac{1}{2}\nabla_i^2 + \sum_A \frac{Z_A}{|\mathbf{r}_i - \mathbf{R}_A|} \qquad \hat{g}(i,j) = \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}$$

and its matrix elements with respect to arbitrary n-electron functions Ψ and Ψ' are given by

$$\begin{aligned}\langle\Psi|\hat{H}_e|\Psi'\rangle &= \sum_i^n \langle\Psi|\hat{h}(i)|\Psi'\rangle + \sum_{i<j}^n \langle\Psi|\hat{g}(i,j)|\Psi'\rangle \\ &= n\langle\Psi|\hat{h}(1)|\Psi'\rangle + \frac{n(n-1)}{2}\langle\Psi|\hat{g}(1,2)|\Psi'\rangle\end{aligned}$$

where the second equality can be shown by exchanging dummy variables ($1 \leftrightarrow i$ and $2 \leftrightarrow j$) in each integral and noting that Ψ and Ψ' are antisymmetric. Then, using the two decompositions shown in equation 4, we can write this as

$$\langle\Psi|\hat{H}_e|\Psi'\rangle = \sum_{pq}^\infty h_{pq}\langle\hat{a}_p\Psi|\hat{a}_q\Psi'\rangle + \frac{1}{2}\sum_{pqrs}^\infty \langle pq|rs\rangle\langle\hat{a}_q\hat{a}_p\Psi|\hat{a}_s\hat{a}_r\Psi'\rangle \qquad h_{pq} = \langle\psi_p(1)|\hat{h}(1)|\psi_q(1)\rangle$$

$$\langle pq|rs\rangle = \langle\psi_p(1)\psi_q(2)|\hat{g}(1,2)|\psi_r(1)\psi_s(2)\rangle$$

where h_{pq} and $\langle pq|rs\rangle$ are our one- and two-electron integrals. Restricting ourselves to the space of m-electron ($m = 0, 1, 2, \ldots, \infty$) functions, we have the identity

$$\hat{H}_e = \sum_{pq}^\infty h_{pq}\hat{a}_p^\dagger\hat{a}_q + \sum_{pqrs}^\infty \langle pq|rs\rangle\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r \tag{5}$$

noting that $\langle\hat{a}_p\Psi|\hat{a}_q\Psi'\rangle = \langle\Psi|\hat{a}_p^\dagger\hat{a}_q\Psi'\rangle$ and $\langle\hat{a}_q\hat{a}_p\Psi|\hat{a}_s\hat{a}_r\Psi'\rangle = \langle\Psi|\hat{a}_p^\dagger\hat{a}_q^\dagger\hat{a}_s\hat{a}_r\Psi'\rangle$ by the definition of adjoint.

[2]Here I'm defining the electronic Hamiltonian as $\hat{H}_e = \hat{H} - (\hat{V}_{\mathrm{Nu}} + \hat{T}_{\mathrm{Nu}})$