Derivation of the Hamiltonian in terms of Unitary Group Generators

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We begin with the second-quantized form of the one- and two-electron operators (see Szabo and Ostlund [1], p. 95),

$$\mathcal{O}_1 = \sum_{ij}^{2K} \langle i|h|j\rangle a_i^\dagger a_j \tag{1}$$

$$\mathcal{O}_2 = \frac{1}{2}\sum_{ijkl}^{2K} \langle ij|kl\rangle a_i^\dagger a_j^\dagger a_l a_k \tag{2}$$

where the sums run over all spin orbitals $\{\chi_i\}$. Thus the Hamiltonian is

$$\hat{H} = \sum_{pq}^{2K} a_p^\dagger a_q [p|h|q] + \frac{1}{2}\sum_{pqrs}^{2K} a_p^\dagger a_r^\dagger a_s a_q [pq|rs] \tag{3}$$

Now integrate over spin, assuming that spatial orbitals are constrained to be identical for α and β spins. A sum over all $2K$ spin orbitals can be split up into two sums, one over K orbitals with α spin, and one over K orbitals with β spin. Symbolically, this is

$$\sum_{a}^{2K} = \sum_{a}^{K} + \sum_{\bar{a}}^{K} \tag{4}$$

The one-electron part of the Hamiltonian becomes

$$\hat{H}_{\text{one}} = \sum_{pq}^{K} [p|h|q] a_{p\alpha}^\dagger a_{q\alpha} + [p|h|\bar{q}] a_{p\alpha}^\dagger a_{q\beta} + [\bar{p}|h|q] a_{p\beta}^\dagger a_{q\alpha} + [\bar{p}|h|\bar{q}] a_{p\beta}^\dagger a_{q\beta} \tag{5}$$

After integrating over spin, this becomes

$$\hat{H}_{\text{one}} = \sum_{pq}^{K} (p|h|q)\{a_{p\alpha}^\dagger a_{q\alpha} + a_{p\beta}^\dagger a_{q\beta}\} \tag{6}$$

The two-electron term can be expanded similarly to give

$$\hat{H}_{\text{two}} = \frac{1}{2}\sum_{pqrs}^{K} (pq|rs)\{a_{p\alpha}^\dagger a_{r\alpha}^\dagger a_{s\alpha} a_{q\alpha} + a_{p\alpha}^\dagger a_{r\beta}^\dagger a_{s\beta} a_{q\alpha} + a_{p\beta}^\dagger a_{r\alpha}^\dagger a_{s\alpha} a_{q\beta} + a_{p\beta}^\dagger a_{r\beta}^\dagger a_{s\beta} a_{q\beta}\} \tag{7}$$

Now we make use of the anticommutation relation

$$\{a_j, a_i\} = a_j a_i + a_i a_j = 0 \tag{8}$$

and we swap the order of $a_{s\alpha}$ and $a_{q\alpha}$, introducing a minus sign. This yields

$$\hat{H}_{\text{two}} = -\frac{1}{2}\sum_{pqrs}^{K}(pq|rs)\{a_{p\alpha}^{\dagger}a_{r\alpha}^{\dagger}a_{q\alpha}a_{s\alpha} + a_{p\alpha}^{\dagger}a_{r\beta}^{\dagger}a_{q\alpha}a_{s\beta} + a_{p\beta}^{\dagger}a_{r\alpha}^{\dagger}a_{q\beta}a_{s\alpha} + a_{p\beta}^{\dagger}a_{r\beta}^{\dagger}a_{q\beta}a_{s\beta}\} \tag{9}$$

Now we use the anticommutation relation between a creation and an annihilation operator, which is

$$\{a_i, a_j^{\dagger}\} = a_i a_j^{\dagger} + a_j^{\dagger} a_i = \delta_{ij} \tag{10}$$

This relation allows us to swap the a_q and $a_r^{\dagger}$ in each term, to give

$$\begin{aligned} \hat{H}_{\text{two}} &= \frac{1}{2}\sum_{pqrs}^{K}(pq|rs)\Big[a_{p\alpha}^{\dagger}a_{q\alpha}a_{r\alpha}^{\dagger}a_{s\alpha} - \delta_{q\alpha,r\alpha}a_{p\alpha}^{\dagger}a_{s\alpha} + a_{p\alpha}^{\dagger}a_{q\alpha}a_{r\beta}^{\dagger}a_{s\beta} - \delta_{q\alpha,r\beta}a_{p\alpha}^{\dagger}a_{s\beta} \\ &+ a_{p\beta}^{\dagger}a_{q\beta}a_{r\alpha}^{\dagger}a_{s\alpha} - \delta_{q\beta,r\alpha}a_{p\beta}^{\dagger}a_{s\alpha} + a_{p\beta}^{\dagger}a_{q\beta}a_{r\beta}^{\dagger}a_{s\beta} - \delta_{q\beta,r\beta}a_{p\beta}^{\dagger}a_{s\beta}\Big] \end{aligned} \tag{11}$$

Now we observe that $\delta_{q\alpha,r\alpha}$ and $\delta_{q\beta,r\beta}$ can both be written δ_{qr}, and also that $\delta_{q\alpha,r\beta}$ and $\delta_{q\beta,r\alpha}$ are both 0. This simplifies our equation to

$$\begin{aligned} \hat{H}_{\text{two}} &= \frac{1}{2}\sum_{pqrs}^{K}(pq|rs)\Big[a_{p\alpha}^{\dagger}a_{q\alpha}a_{r\alpha}^{\dagger}a_{s\alpha} + a_{p\alpha}^{\dagger}a_{q\alpha}a_{r\beta}^{\dagger}a_{s\beta} + a_{p\beta}^{\dagger}a_{q\beta}a_{r\alpha}^{\dagger}a_{s\alpha} + a_{p\beta}^{\dagger}a_{q\beta}a_{r\beta}^{\dagger}a_{s\beta} \\ &- \delta_{qr}a_{p\alpha}^{\dagger}a_{s\alpha} - \delta_{qr}a_{p\beta}^{\dagger}a_{s\beta}\Big] \end{aligned} \tag{12}$$

Now we introduce the unitary group generators, which we write as [2]

$$\hat{E}_{ij} = a_{i\alpha}^{\dagger}a_{j\alpha} + a_{i\beta}^{\dagger}a_{j\beta} \tag{13}$$

and the Hamiltonian becomes

$$\hat{H} = \sum_{pq}^{K}(p|h|q)\hat{E}_{pq} + \frac{1}{2}\sum_{pqrs}^{K}(pq|rs)\left(\hat{E}_{pq}\hat{E}_{rs} - \delta_{qr}\hat{E}_{ps}\right) \tag{14}$$

This is the Hamiltonian in terms of the unitary group generators [3].

References

[1] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. McGraw-Hill, New York, 1989.

[2] J. Paldus, J. Chem. Phys. **61**, 5321 (1974).

[3] I. Shavitt, Int. J. Quantum Chem. Symp. **12**, 5 (1978).