Handout 6 (read by Nov. 27)

Example 2.2.22 from QM.
Consider the Hamilton operator of a two-electron system in the Coulomb field of a nucleus with charge Ze, $e > 0$ (see, e.g., G. K. Woodgate, Elementary atomic structure, Clarendon Press, Oxford, 1983, chapter 5):

$$H = \underbrace{\frac{\vec{p}^{\,2}(1)}{2m} + V_1(r(1))}_{H_0(1)} + \underbrace{\frac{\vec{p}^{\,2}(2)}{2m} + V_1(r(2))}_{H_0(2)} + V_2(r_{12}) =: H_0 + V_2$$

with $(n = 1, 2)$

$$\begin{aligned} r(n) &= |\vec{r}(n)|, & r_{12} &= |\vec{r}(1) - \vec{r}(2)|, \\ V_1(r(n)) &= -\frac{Ze^2}{4\pi r(n)}, & V_2(r_{12}) &= \frac{e^2}{4\pi r_{12}}. \end{aligned}$$

The commutation relations for the components of the position and momentum operators read $(m, n \in \{1, 2\};\ i, j \in \{1, 2, 3\})$:

$$\begin{aligned} [x_i(m), x_j(n)] &= 0, \\ [p_i(m), p_j(n)] &= 0, \\ [x_i(m), p_j(n)] &= i\delta_{ij}\delta_{mn}. \end{aligned}$$

- If we neglect the interaction between the two electrons, the system is described by the Hamilton operator $H_0 = H_0(1) + H_0(2)$, which has a $G = \mathrm{O}(3) \times \mathrm{O}(3)$ symmetry. By this we mean, that the Hamilton operator is invariant under independent transformations of the operators of particle 1 and of particle 2, respectively,

  $$\begin{aligned} x_i'(1) &= R_{ij}(1)x_j(1), \quad p_i'(1) = R_{ij}(1)p_j(1), \quad R(1) \in \mathrm{O}(3), \\ x_i'(2) &= R_{ij}(2)x_j(2), \quad p_i'(2) = R_{ij}(2)p_j(2), \quad R(2) \in \mathrm{O}(3). \end{aligned}$$

  There is no need to choose $R(1) = R(2)$ and, therefore, the symmetry group is the external direct product $\mathrm{O}(3) \times \mathrm{O}(3)$.

- The Hamilton operators $H_0(1)$ and $H_0(2)$ commute. Therefore, a product ansatz is made for the solutions of the stationary Schrödinger equation. Using Dirac's bra-ket notation, the eigenstates are of the type[1]

  $$|n_1, l_1, m_1\rangle \otimes |n_2, l_2, m_2\rangle,$$

  where $\{|l_i, m_i\rangle | m_i = -l_i, \ldots, l_i\}$, $l_i \in \mathbb{N}_0$, are bases of the carrier spaces of irreducible representations $D^{(l_i)}$ of SO(3). If $|V_2| \ll |H_0|$, one makes use of $|l_1, m_1\rangle \otimes |l_2, m_2\rangle$ as the starting point of perturbation theory.

[1] For the moment, we omit the electron spin and also neglect the Pauli principle, which is enforced in terms of a totally antisymmetric wavefunction.

- Let us define $G' := \{(g, g) | g \in \mathrm{O}(3)\} \cong \mathrm{O}(3)$. The Hamilton operator $H = H_0 + V_2$ has a lower symmetry than H_0, because $G' < G$. This reduction in symmetry originates from the fact that (exercise)

$$[\ell_i(n), V_2(r_{12})] \neq 0,$$

i.e., the individual angular momenta are no longer conserved quantities. On the other hand,

$$[L_i, V_2(r_{12})] = 0$$

with $\vec{L} = \vec{\ell}(1) + \vec{\ell}(2)$ $(= \vec{\ell} \otimes I + I \otimes \vec{\ell})$, such that the total angular momentum is still a conserved quantity. The eigenstates of H may be classified with respect to the total angular momentum, where

$$\{|L, M\rangle, M = -L, \ldots, L\}$$

is the basis of the carrier space of an irreducible representation $D^{(L)}$ of SO(3). The interaction between the two electrons, V_2, leads to a (partial) removal of the degeneracy of the energy levels of H_0, because H has a lower symmetry than H_0.