Project - FYS4411

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February 8, 2014

Abstract

1 The Hartree-Fock method

1.1 Approximations

There are five main approximations in the Hartree-Fock method:

- The Born-Oppenheimer approximation
- Relativistic effects are neglected
- The solution is a linear combination of (typically orthogonal) basis functions
- Each energy eigenfunction is assumed to be describable by a single Slater determinant
- The mean field approximation is implied.

The Hartree equation in atomic units:

$$\left[-\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\mathbf{r}-\mathbf{R}_n|} + \sum_{l=1}^{N}\int \mathrm{d}x'|\psi_l(\mathbf{x})|^2\frac{1}{|\mathbf{r}-\mathbf{r}'|}\right]\psi_k(\mathbf{x}) = E'\psi_k(\mathbf{x}) \quad (1)$$

Note that $\mathbf{x}' = (\mathbf{r}', s')$, so that $\int \mathrm{d}x' = \sum_{s'}\int \mathrm{d}\mathbf{r}'$.
The last term on the left side is called the *Hartree potential*.

1.2 The Slater determinant

Since electrons are indistinguishable, the Hamiltonian commites with the particle-exchange operator P_{ij}:

$$\mathbf{P}_{ij}\Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_i, ..., \mathbf{x}_j, ...\mathbf{x}_N) = \Psi(\mathbf{x}_1, \mathbf{x}_2, ..., \mathbf{x}_j, ..., \mathbf{x}_i, ...\mathbf{x}_N) \quad (2)$$

The eigenvalue of P is -1 (experimental) for fermions. We are working with an independent-particle Hamiltonian, so the electron state can be written as a product of single-electron states:

$$\Psi(\mathbf{x}_1, ..., \mathbf{x}_N) = \psi_1(\mathbf{x}_1)\cdots\psi_N(\mathbf{x}_N) \quad (3)$$