Part 1

Born-Oppenheimer approximation: Treat heavy nuclei as fixed points and we want to only solve the ground state problem for the electrons

All energies are given in Hartrees ($1H = 27.2114eV$) and distances are given in Bohr radii ($a_0 = 0.529 \text{ Å}$).

For larger systems with N electrons the wave function depends on all $3N$ coordinates of those electrons.

With an exact ground state wavefunction it is easy to calculate the probability density of the system:

$$n(\underline{r}) = 2\int d^3\underline{r}' \, |\Psi(\underline{r}, \underline{r}')|^2$$

This says that the probability of finding an electron in $d^3\underline{r}$ around $\underline{r}$ is $n(\underline{r})d^3\underline{r}$.

Now if we imagine a system of two non-interacting electrons in a potential $V_S(\underline{r})$ that is chosen to mimic the true electron system. Since they are non interacting their coordinates decouple and their wavefunction is a product of one-electron wave functions. Since they are non interacting for a system of N electrons we only need to solve a 3d equation.

The Hartree-Fock equations are one approach to mimic the interacting system to the non interacting one:

$$V_S^{HF}(\underline{r}) = V_{ext}(\underline{r}) + \underbrace{\frac{1}{2}\int d^3\underline{r}' \frac{n(\underline{r}')}{|\underline{r} - \underline{r}'|}}$$

This added correction mimics the effect of the second electron

The Hartree-Focks main pitfall is that it significantly underbinds the molecule. The extra energy needed is called the correlation energy.