

26.3: Solving the Electronic Eigenvalue Problem

Once we have invoked the Born-Oppenheimer approximation, we can attempt to solve the electronic TISEq in [Equation 27.2.7](#). However, for molecules with more than one electron, we need to—once again—keep in mind the antisymmetry of the wave function. This obviously means that we need to write the electronic wave function as a Slater determinant (i.e., all molecules but H_2^+ and a few related highly exotic ions). Once this is done, we can work on approximating the Hamiltonian, a task that is necessary because the presence of the electron-electron repulsion term forbids its analytic treatment. Similarly to the many-electron atom case, the simplest approximation to solve the molecular electronic TISEq is to use the variational method and to neglect the electron-electron repulsion. As we noticed in the previous chapter, this approximation is called the Hartree-Fock method.

The Hartree-Fock Method

The main difference when we apply the variational principle to a molecular Slater determinant is that we need to build orbitals (one-electron wave functions) that encompass the entire molecule. This can be done by assuming that the atomic contributions to the molecular orbitals will closely resemble the orbitals that we obtained for the hydrogen atom. The total molecular orbital can then be built by linearly combine these atomic contributions. This method is called **linear combination of atomic orbitals (LCAO)**. A consequence of the LCAO method is that the atomic orbitals on two different atomic centers are not necessarily orthogonal, and [Equation 26.2.4](#) cannot be simplified easily. If we replace each atomic orbital $\psi(\mathbf{r})$ with a linear combination of suitable basis functions $f_i(\mathbf{r})$:

$$\psi(\mathbf{r}) = \sum_i^m c_i f_i(\mathbf{r}), \quad (26.3.1)$$

we can then use the following notation:

$$H_{ij} = \int \phi_i^* \hat{H} \phi_j d\tau, \quad S_{ij} = \int \phi_i^* \phi_j d\tau, \quad (26.3.2)$$

to simplify [Equation 26.2.4](#) to:

$$E[\Phi] = \frac{\sum_{ij} c_i^* c_j H_{ij}}{\sum_{ij} c_i^* c_j S_{ij}}. \quad (26.3.3)$$

Differentiating this energy with respect to the expansion coefficients c_i yields a non-trivial solution only if the following “secular determinant” equals zero:

$$\begin{vmatrix} H_{11} - ES_{11} & H_{12} - ES_{12} & \cdots & H_{1m} - ES_{1m} \\ H_{21} - ES_{21} & H_{22} - ES_{22} & \cdots & H_{2m} - ES_{2m} \\ \vdots & \vdots & \ddots & \vdots \\ H_{m1} - ES_{m1} & H_{m2} - ES_{m2} & \cdots & H_{mm} - ES_{mm} \end{vmatrix} = 0 \quad (26.3.4)$$

where m is the number of basis functions used to expand the atomic orbitals. Solving this set of equations with a Hamiltonian where the electron-electron correlation is neglected results is non-trivial, but possible. The reason for the complications comes from the fact that even if we are neglecting the direct interaction between electrons, each of them interact with the nuclei through an interaction that is screened by the average field of all other electrons, similarly to what we saw for the helium atom. This means that the Hamiltonian itself and the value of the coefficients c_i in the wave function mutually depend on each other. A solution to this problem can be achieved numerically using specialized computer programs that use a cycle called the **self-consistent-field (SCF) procedure**. Starting from an initial guess of the coefficients, an approximated Hamiltonian operator is built from them and used to solve [Equation 26.3.4](#). This solution gives updated values of the coefficients, which can then be used to create an improved version of the approximated Hamiltonian. This procedure is repeated until both the coefficients and the operator do not change anymore. From this final solution, the energy of the molecule is then calculated.

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