

## 25.2: Approximated Hamiltonians

In order to solve the TISEq for a many-electron atom we also need to approximate the Hamiltonian, since analytic solution using the full Hamiltonian as in Equation 26.1 are impossible to find. The most significant approximation used in chemistry is called the *variational method*.

### Variational method

The basic idea of the variational method is to guess a “trial” wave function for the problem consisting of some adjustable parameters called “variational parameters”. These parameters are adjusted until the energy of the trial wave function is minimized. The resulting trial wave function and its corresponding energy are variational method approximations to the exact wave function and energy.

Why would it make sense that the best approximate trial wave function is the one with the lowest energy? This results from the Variational Theorem, which states that the energy of any trial wave function  $E$  is always an upper bound to the exact ground state energy  $\mathcal{E}_0$ . This can be proven easily. Let the trial wave function be denoted  $\Phi$ . Any trial function can formally be expanded as a linear combination of the exact eigenfunctions  $\Psi_i$ . Of course, in practice, we don’t know the  $\Psi_i$ , since we are applying the variational method to a problem we can’t solve analytically. Nevertheless, that doesn’t prevent us from using the exact eigenfunctions in our proof, since they certainly exist and form a complete set, even if we don’t happen to know them. So, the trial wave function can be written:

$$\Phi = \sum_i c_i \Psi_i, \quad (25.2.1)$$

and the approximate energy corresponding to this wave function is:

$$E[\Phi] = \frac{\int \Phi^* \hat{H} \Phi d\tau}{\int \Phi^* \Phi d\tau}, \quad (25.2.2)$$

where  $\tau = (\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$  is the ensemble of the spatial coordinates of each electron and the integral symbol is assumed as a  $3N$ -dimensional integration. Replacing the expansion over the exact wave functions, we obtain:

$$E[\Phi] = \frac{\sum_{ij} c_i^* c_j \int \Psi_i^* \hat{H} \Psi_j d\tau}{\sum_{ij} c_i^* c_j \int \Psi_i^* \Psi_j d\tau}. \quad (25.2.3)$$

Since the functions  $\Psi_j$  are the exact eigenfunctions of  $\hat{H}$ , we can use  $\hat{H} \Psi_j = \mathcal{E}_j \Psi_j$  to obtain:

$$E[\Phi] = \frac{\sum_{ij} c_i^* c_j \mathcal{E}_j \int \Psi_i^* \Psi_j d\tau}{\sum_{ij} c_i^* c_j \int \Psi_i^* \Psi_j d\tau}. \quad (25.2.4)$$

Now using the fact that eigenfunctions of a Hermitian operator form an orthonormal set (or can be made to do so), we can write:

$$E[\Phi] = \frac{\sum_i c_i^* c_i \mathcal{E}_i}{\sum_i c_i^* c_i}. \quad (25.2.5)$$

We now subtract the exact ground state energy  $\mathcal{E}_0$  from both sides to obtain

$$E[\Phi] - \mathcal{E}_0 = \frac{\sum_i c_i^* c_i (\mathcal{E}_i - \mathcal{E}_0)}{\sum_i c_i^* c_i}. \quad (25.2.6)$$

Since every term on the right-hand side is greater than or equal to zero, the left-hand side must also be greater than or equal to zero:

$$E[\Phi] \geq \mathcal{E}_0. \quad (25.2.7)$$

In other words, the energy of any approximate wave function is always greater than or equal to the exact ground state energy  $\mathcal{E}_0$ .

This explains the strategy of the variational method: since the energy of any approximate trial function is always above the true energy, then any variations in the trial function which lower its energy are necessarily making the approximate energy closer to the exact answer. (The trial wave function is also a better approximation to the true ground state wave function as the energy is lowered, although not necessarily in every possible sense unless the limit  $\Phi = \Psi_0$  is reached).

## Approximated solution for the helium atom

We now have all the ingredients to attempt the simplest approximated solution to the TISEq of a many-electron atom. We can start by writing the total wave function using the Slater determinant of [Equation 26.1.7](#) in terms of spin-orbitals:

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = |\chi_1, \chi_2, \dots, \chi_N\rangle = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1 \phi_\uparrow & \psi_1 \phi_\downarrow & \dots & \psi_N \phi_\uparrow & \psi_N \phi_\downarrow \end{vmatrix}, \quad (25.2.8)$$

and then we can replace it into the TISEq for an  $N$ -electron system. This results into a set of  $N$  one-electron equations, one for each electron. When we attempt to solve each individual equation, however, we end up with a problem, since the potential energy in the Hamiltonian of [Equation 26.1](#) does not have spherical symmetry because of the electron-electron repulsion term. As such, the one-electron TISEq cannot be simply solved in spherical polar coordinates, as we did for the hydrogen atom in [chapter 21](#). The simplest way of circumventing the problem is to neglect the electron-electron repulsion term (i.e., assume that the electrons are not correlated and do not interact with each other). For a 2-electron atom this procedure is straightforward, since the Hamiltonian can be written as a sum of one-electron Hamiltonians:

$$\hat{H} = \hat{H}_1 + \hat{H}_2, \quad (25.2.9)$$

with  $\hat{H}_1$  and  $\hat{H}_2$  looking identical to those used in the TISEq of the hydrogen atom. This one-particle Hamiltonian does not depend on the spin of the electron, and therefore, we can neglect the spin component of the Slater determinant and write the total wave function for the ground state of helium, Equation 26.1.4, simply as:

$$\Psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_{100}(\mathbf{r}_1)\psi_{100}(\mathbf{r}_2). \quad (25.2.10)$$

The overall TISEq reduces to a set of two single-particle equations:

$$\begin{aligned} \hat{H}_1 \psi_{100}(\mathbf{r}_1) &= E_1 \psi_{100}(\mathbf{r}_1) \\ \hat{H}_2 \psi_{100}(\mathbf{r}_2) &= E_2 \psi_{100}(\mathbf{r}_2), \end{aligned}$$

which can then be solved similarly to those for the hydrogen atom, and the solution be combined to give:

$$E = E_1 + E_2. \quad (25.2.11)$$

In other words, the resulting energy eigenvalue for the ground state of the helium atom in this approximation is equal to twice the energy of a  $\psi_{100}$ ,  $1s$ , orbital. The resulting approximated value for the energy of the helium atom is 7,217 kJ/mol, compared with the exact value of 7,620 kJ/mol

The nuclear charge  $Z$  in the  $\psi_{100}$  orbital can be used as a variational parameter in the variational method to obtain a more accurate value of the energy. This method provides a result for the ground-state energy of the helium atom of 7,478 kJ/mol (only 142 kJ/mol lower than the exact value), with the nuclear charge parameter minimized at  $Z_{\min} = 1.6875$ . This new value of the nuclear charge can be interpreted as the effective nuclear charge that is felt by one electron when a second electron is present in the atom. This value is lower than the real nuclear charge ( $Z = 2$ ) because the interaction between the electron and the nuclei is shielded by presence of the second electron.

This procedure can be extended to atoms with more than two electrons, resulting in the so-called Hartree-Fock method. The procedure, however, is not straightforward. We will explain it in more details in the next chapter, since it is the simplest approximation that also describes the chemical bond.

---

This page titled [25.2: Approximated Hamiltonians](#) is shared under a [CC BY-SA 4.0](#) license and was authored, remixed, and/or curated by [Roberto Peverati](#).