

9.3: Perturbation Theory

Perturbation theory is a method for continuously improving a previously obtained approximate solution to a problem, and it is an important and general method for finding approximate solutions to the Schrödinger equation. We discussed a simple application of the perturbation technique previously with the [Zeeman effect](#).

We use perturbation theory to approach the analytically unsolvable helium atom Schrödinger equation by focusing on the Coulomb repulsion term that makes it different from the simplified Schrödinger equation that we have just solved analytically. The electron-electron repulsion term is conceptualized as a correction, or perturbation, to the Hamiltonian that can be solved exactly, which is called a zero-order Hamiltonian. The perturbation term corrects the previous Hamiltonian to make it fit the new problem. In this way the Hamiltonian is built as a sum of terms, and each term is given a name. For example, we call the simplified or starting Hamiltonian, \hat{H}^0 , the zero order term, and the correction term \hat{H}^1 , the first order term. In the general expression below, there can be an infinite number of correction terms of increasingly higher order,

$$\hat{H} = \hat{H}^0 + \hat{H}^1 + \hat{H}^2 + \dots \quad (9.3.1)$$

but usually it is not necessary to have more terms than \hat{H}^0 and \hat{H}^1 . For the helium atom,

$$\hat{H}^0 = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{2e^2}{4\pi\epsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{2e^2}{4\pi\epsilon_0 r_2} \quad (9.3.2)$$

$$\hat{H}^1 = \frac{2e^2}{4\pi\epsilon_0 r_{12}} \quad (9.3.3)$$

In the general form of perturbation theory, the wavefunctions are also built as a sum of terms, with the zero-order terms denoting the exact solutions to the zero-order Hamiltonian and the higher-order terms being the corrections.

$$\psi = \psi^0 + \psi^1 + \psi^2 + \dots \quad (9.3.4)$$

Similarly, the energy is written as a sum of terms of increasing order.

$$E = E^0 + E^1 + E^2 + \dots \quad (9.3.5)$$

To solve a problem using perturbation theory, you start by solving the zero-order equation. This provides an approximate solution consisting of E_0 and ψ^0 . The zero-order perturbation equation for the helium atom is

$$\hat{H}^0 \psi^0 = E^0 \psi^0 \quad (9.3.6)$$

We already solved this equation for the helium atom and found that $E_0 = -108$ eV by using the product of two hydrogen atom wavefunctions for ψ^0 and omitting the electron-electron interaction from \hat{H}^0 .

The next step is to improve upon the zero-order solution by including \hat{H}^1 , \hat{H}^2 etc. and finding ψ^1 and E_1 , ψ^2 and E_2 , etc. The solution is improved through the stepwise addition of other functions to the previously found result. These functions are found by solving a series of Schrödinger-like equations, the higher-order perturbation equations.

The first-order perturbation equation includes all the terms in the Schrödinger equation $\hat{H}\psi = E\psi$ that represent the first order approximations to \hat{H} , ψ and E . This equation can be obtained by truncating \hat{H} , ψ and E after the first order terms.

$$(\hat{H}^0 + \hat{H}^1)(\psi^0 + \psi^1) = (E^0 + E^1)(\psi^0 + \psi^1) \quad (9.3.7)$$

Now clear the parentheses to get

$$\hat{H}^0 \psi^0 + \hat{H}^0 \psi^1 + \hat{H}^1 \psi^0 + \hat{H}^1 \psi^1 = E^0 \psi^0 + E^0 \psi^1 + E^1 \psi^0 + E^1 \psi^1 \quad (9.3.8)$$

The order of the perturbation equation matches the sum of the superscripts for a given term in the equation above. To form the first-order perturbation equation, we can drop the $\hat{H}^0 \psi^0$ and $E^0 \psi^0$ terms because they are zero-order terms and because they cancel each other out, as shown by Equation 9.3.6 We can also drop the $\hat{H}^1 \psi^1$ and $E^1 \psi^1$ terms because they are second-order corrections formed by a product of two first-order corrections. The first order perturbation equation thus is

$$\hat{H}^0 \psi^1 + \hat{H}^1 \psi^0 = E^0 \psi^1 + E^1 \psi^0 \quad (9.3.9)$$

To find the first order correction to the energy take the first-order perturbation equation, multiply from the left by ψ^{0*} and integrate over all the coordinates of the problem at hand.

$$\int \psi^{0*} \hat{H}^0 \psi^1 d\tau + \int \psi^{0*} \hat{H}^1 \psi^0 d\tau = E^0 \int \psi^{0*} \psi^1 d\tau + E^1 \int \psi^{0*} \psi^0 d\tau \quad (9.3.10)$$

The integral in the last term on the right hand side of Equation 9.3.10 is equal to one because the wavefunctions are normalized. Because \hat{H}^0 is Hermitian, the first integral in Equation 9.3.10 can be rewritten to make use of Equation 9.3.6,

$$\int \psi^{0*} \hat{H}^0 \psi^1 d\tau = \int (\hat{H}^{0*} \psi^{0*}) \psi^1 d\tau = E^0 \int \psi^{0*} \psi^1 d\tau \quad (9.3.11)$$

which is the same as and therefore cancels the first integral on the right-hand side. Thus we are left with an expression for the first-order correction to the energy

$$E^1 = \int \psi^{0*} \hat{H}^1 \psi^0 d\tau \quad (9.3.12)$$

Since the derivation above was completely general, Equation 9.3.12 is a general expression for the first-order perturbation energy, which provides an improvement or correction to the zero-order energy we already obtained. The integral on the right is in fact an expectation value integral in which the zero-order wavefunctions are operated on by \hat{H}^1 , the first-order perturbation term in the Hamiltonian, to calculate the expectation value for the first-order energy. This derivation justifies, for example, the method we used for the Zeeman effect to approximate the energies of the hydrogen atom orbitals in a magnetic field. Recall that we calculated the expectation value for the interaction energy (the first-order correction to the energy) using the exact hydrogen atom wavefunctions (the zero-order wavefunctions) and a Hamiltonian operator representing the magnetic field perturbation (the first-order Hamiltonian term.)

Exercise 9.3.7

Without using mathematical expressions, explain how you would solve Equation 9.3.12 for the first-order energy.

For the helium atom, the integral in Equation 9.3.12 is

$$E^1 = \iint \varphi_{1s}(r_1) \varphi_{1s}(r_2) \frac{1}{r_{12}} \varphi_{1s}(r_1) \varphi_{1s}(r_2) d\tau_1 d\tau_2 \quad (9.3.13)$$

where the double integration symbol represents integration over all the spherical polar coordinates of both electrons $r_1, \theta_1, \varphi_1, r_2, \theta_2, \varphi_2$. The evaluation of these six integrals is lengthy. When the integrals are done, the result is $E^1 = +34.0$ eV so that the total energy calculated using our second approximation method, first-order perturbation theory, is

$$E_{approx2} = E^0 + E^1 = -74.8 \text{ eV} \quad (9.3.14)$$

E^1 is the **average interaction energy** of the two electrons calculated using wavefunctions that assume there is no interaction.

The new approximate value for the binding energy represents a substantial (~30%) improvement over the zero-order energy, so the interaction of the two electrons is an important part of the total energy of the helium atom. We can continue with perturbation theory and find the additional corrections, E^2, E^3 , etc. For example, $E^0 + E^1 + E^2 = -79.2$ eV. So with two corrections to the energy, the calculated result is within 0.3% of the experimental value of -79.00 eV. It takes thirteenth-order perturbation theory (adding E^1 through E^{13} to E^0) to compute an energy for helium that agrees with experiment to within the experimental uncertainty.

Interestingly, while we have improved the calculated energy so that it is much closer to the experimental value, we learn nothing new about the helium atom wavefunction by applying the first-order perturbation theory because we are left with the original zero-order wavefunctions. In the next section we will employ an approximation that modifies zero-order wavefunctions in order to address one of the ways that electrons are expected to interact with each other.

Contributors and Attributions

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