

13.2: Helium Atom

A helium atom consists of a nucleus of charge $+2e$ surrounded by two electrons. Let us attempt to calculate its ground-state energy.

Let the nucleus lie at the origin of our coordinate system, and let the position vectors of the two electrons be \mathbf{r}_1 and \mathbf{r}_2 , respectively. The Hamiltonian of the system thus takes the form

$$H = -\frac{\hbar^2}{2m_e}(\nabla_1^2 + \nabla_2^2) - \frac{e^2}{4\pi\epsilon_0}\left(\frac{2}{r_1} + \frac{2}{r_2} - \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|}\right), \quad (13.2.1)$$

where we have neglected any reduced mass effects. The terms in the previous expression represent the kinetic energy of the first electron, the kinetic energy of the second electron, the electrostatic attraction between the nucleus and the first electron, the electrostatic attraction between the nucleus and the second electron, and the electrostatic repulsion between the two electrons, respectively. It is the final term that causes all of the difficulties. Indeed, if this term is neglected then we can write

$$H = H_1 + H_2, \quad (13.2.2)$$

where

$$H_{1,2} = -\frac{\hbar^2}{2m_e}\nabla_{1,2}^2 - \frac{2e^2}{4\pi\epsilon_0 r_{1,2}}. \quad (13.2.3)$$

In other words, the Hamiltonian just becomes the sum of separate Hamiltonians for each electron. In this case, we would expect the wavefunction to be separable: that is,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_1(\mathbf{r}_1)\psi_2(\mathbf{r}_2). \quad (13.2.4)$$

Hence, Schrödinger's equation,

$$H\psi = E\psi, \quad (13.2.5)$$

reduces to

$$H_{1,2}\psi_{1,2} = E_{1,2}\psi_{1,2}, \quad (13.2.6)$$

where

$$E = E_1 + E_2. \quad (13.2.7)$$

Of course, Equation ??? is the Schrödinger equation of a hydrogen atom whose nuclear charge is $+2e$, instead of $+e$. It follows, from Section [s10.4] (making the substitution $e^2 \rightarrow 2e^2$), that if both electrons are in their lowest energy states then

$$\begin{aligned} \psi_1(\mathbf{r}_1) &= \psi_0(\mathbf{r}_1), \\ \psi_2(\mathbf{r}_2) &= \psi_0(\mathbf{r}_2), \end{aligned}$$

where

$$\psi_0(\mathbf{r}) = \frac{4}{\sqrt{2\pi}a_0^{3/2}}\exp\left(-\frac{2r}{a_0}\right). \quad (13.2.8)$$

Here, a_0 is the Bohr radius. [See Equation ([e9.57]).] Note that ψ_0 is properly normalized. Furthermore,

$$E_1 = E_2 = 4E_0, \quad (13.2.9)$$

where $E_0 = -13.6$ eV is the hydrogen ground-state energy. [See Equation ([e9.56]).] Thus, our crude estimate for the ground-state energy of helium becomes

$$E = 4E_0 + 4E_0 = 8E_0 = -108.8 \text{ eV}. \quad (13.2.10)$$

Unfortunately, this estimate is significantly different from the experimentally determined value, which is -78.98 eV. This fact demonstrates that the neglected electron-electron repulsion term makes a large contribution to the helium ground-state energy. Fortunately, however, we can use the variational principle to estimate this contribution.

Let us employ the separable wavefunction discussed previously as our trial solution. Thus,

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi_0(\mathbf{r}_1) \psi_0(\mathbf{r}_2) = \frac{8}{\pi a_0^3} \exp\left(-\frac{2[r_1 + r_2]}{a_0}\right). \quad (13.2.11)$$

The expectation value of the Hamiltonian 13.2.1 thus becomes

$$\langle H \rangle = 8 E_0 + \langle V_{ee} \rangle, \quad (13.2.12)$$

where

$$\langle V_{ee} \rangle = \left\langle \psi \left| \frac{e^2}{4\pi \epsilon_0 |\mathbf{r}_2 - \mathbf{r}_1|} \right| \psi \right\rangle = \frac{e^2}{4\pi \epsilon_0} \int \frac{|\psi(\mathbf{r}_1, \mathbf{r}_2)|^2}{|\mathbf{r}_2 - \mathbf{r}_1|} d^3 \mathbf{r}_1 d^3 \mathbf{r}_2. \quad (13.2.13)$$

The variation principle only guarantees that Equation 13.2.12 yields an upper bound on the ground-state energy. In reality, we hope that it will give a reasonably accurate estimate of this energy.

It follows from Equations ([e9.56]), 13.2.11, and 13.2.13 that

$$\langle V_{ee} \rangle = -\frac{4 E_0}{\pi^2} \int \frac{e^{-2(\hat{r}_1 + \hat{r}_2)}}{|\hat{\mathbf{r}}_1 - \hat{\mathbf{r}}_2|} d^3 \hat{\mathbf{r}}_1 d^3 \hat{\mathbf{r}}_2, \quad (13.2.14)$$

where $\hat{\mathbf{r}}_{1,2} = 2 \mathbf{r}_{1,2}/a_0$. Neglecting the hats, for the sake of clarity, the previous expression can also be written

$$\langle V_{ee} \rangle = -\frac{4 E_0}{\pi^2} \int \frac{e^{-2(r_1 + r_2)}}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta}} d^3 \mathbf{r}_1 d^3 \mathbf{r}_2, \quad (13.2.15)$$

where θ is the angle subtended between vectors \mathbf{r}_1 and \mathbf{r}_2 . If we perform the integral in \mathbf{r}_1 space before that in \mathbf{r}_2 space then

$$\langle V_{ee} \rangle = -\frac{4 E_0}{\pi^2} \int e^{-2 r_2} I(\mathbf{r}_2) d^3 \mathbf{r}_2, \quad (13.2.16)$$

where

$$I(\mathbf{r}_2) = \int \frac{e^{-2 r_1}}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta}} d^3 \mathbf{r}_1. \quad (13.2.17)$$

Our first task is to evaluate the function $I(\mathbf{r}_2)$. Let (r_1, θ_1, ϕ_1) be a set of spherical coordinates in \mathbf{r}_1 space whose axis of symmetry runs in the direction of \mathbf{r}_2 . It follows that $\theta = \theta_1$. Hence,

$$I(\mathbf{r}_2) = \int_0^\infty \int_0^\pi \int_0^{2\pi} \frac{e^{-2 r_1}}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta_1}} r_1^2 dr_1 \sin \theta_1 d\theta_1 d\phi_1, \quad (13.2.18)$$

which trivially reduces to

$$I(\mathbf{r}_2) = 2\pi \int_0^\infty \int_0^\pi \frac{e^{-2 r_1}}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta_1}} r_1^2 dr_1 \sin \theta_1 d\theta_1. \quad (13.2.19)$$

Making the substitution $\mu = \cos \theta_1$, we can see that

$$\int_0^\pi \frac{1}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \cos \theta_1}} \sin \theta_1 d\theta_1 = \int_{-1}^1 \frac{d\mu}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \mu}}. \quad (13.2.20)$$

Now,

$$\begin{aligned}\int_{-1}^1 \frac{d\mu}{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \mu}} &= \left[\frac{\sqrt{r_1^2 + r_2^2 - 2 r_1 r_2 \mu}}{r_1 r_2} \right]_{-1}^{-1} \\ &= \frac{(r_1 + r_2) - |r_1 - r_2|}{r_1 r_2} \\ &= \begin{cases} 2/r_1 & \text{for } r_1 > r_2 \\ 2/r_2 & \text{for } r_1 < r_2 \end{cases},\end{aligned}$$

giving

$$I(\mathbf{r}_2) = 4\pi \left(\frac{1}{r_2} \int_0^{r_2} e^{-2r_1} r_1^2 dr_1 + \int_{r_2}^{\infty} e^{-2r_1} r_1 dr_1 \right). \quad (13.2.21)$$

But ,

$$\begin{aligned}\int e^{-\beta x} x dx &= -\frac{e^{-\beta x}}{\beta^2} (1 + \beta x), \\ \int e^{-\beta x} x^2 dx &= -\frac{e^{-\beta x}}{\beta^3} (2 + 2\beta x + \beta^2 x^2),\end{aligned}$$

yielding

$$I(\mathbf{r}_2) = \frac{\pi}{r_2} [1 - e^{-2r_2} (1 + r_2)]. \quad (13.2.22)$$

Because the function $I(\mathbf{r}_2)$ only depends on the magnitude of \mathbf{r}_2 , the integral in Equation 13.2.16 reduces to

$$\langle V_{ee} \rangle = -\frac{16 E_0}{\pi} \int_0^{\infty} e^{-2r_2} I(r_2) r_2^2 dr_2, \quad (13.2.23)$$

which yields

$$\langle V_{ee} \rangle = -16 E_0 \int_0^{\infty} e^{-2r_2} [1 - e^{-2r_2} (1 + r_2)] r_2 dr_2 = -\frac{5}{2} E_0. \quad (13.2.24)$$

Hence, from Equation 13.2.12 our estimate for the ground-state energy of helium is

$$\langle H \rangle = 8 E_0 - \frac{5}{2} E_0 = \frac{11}{2} E_0 = -74.8 \text{ eV}. \quad (13.2.25)$$

This is remarkably close to the correct result.

Shielding and Effective Nuclear Charge

We can actually refine our estimate further. The trial wavefunction 13.2.11 essentially treats the two electrons as non-interacting particles. In reality, we would expect one electron to partially shield the nuclear charge from the other, and vice versa. Hence, a better trial wavefunction might be

$$\psi(\mathbf{r}_1, \mathbf{r}_2) = \frac{Z^3}{\pi a_0^3} \exp\left(-\frac{Z[r_1 + r_2]}{a_0}\right), \quad (13.2.26)$$

where $Z < 2$ is effective nuclear charge number seen by each electron. Let us recalculate the ground-state energy of helium as a function of Z , using the previous trial wavefunction, and then minimize the result with respect to Z . According to the variational principle, this should give us an even better estimate for the ground-state energy.

We can rewrite the expression 13.2.1 for the Hamiltonian of the helium atom in the form

$$H = H_1(Z) + H_2(Z) + V_{ee} + U(Z), \quad (13.2.27)$$

where

$$H_{1,2}(Z) = -\frac{\hbar^2}{2m_e} \nabla_{1,2}^2 - \frac{Ze^2}{4\pi\epsilon_0 r_{1,2}} \quad (13.2.28)$$

is the Hamiltonian of a hydrogen atom with nuclear charge $+Ze$,

$$V_{ee} = \frac{e^2}{4\pi\epsilon_0} \frac{1}{|\mathbf{r}_2 - \mathbf{r}_1|} \quad (13.2.29)$$

is the electron-electron repulsion term, and

$$U(Z) = \frac{e^2}{4\pi\epsilon_0} \left(\frac{[Z-2]}{r_1} + \frac{[Z-2]}{r_2} \right). \quad (13.2.30)$$

It follows that

$$\langle H \rangle(Z) = 2E_0(Z) + \langle V_{ee} \rangle(Z) + \langle U \rangle(Z), \quad (13.2.31)$$

where $E_0(Z) = Z^2 E_0$ is the ground-state energy of a hydrogen atom with nuclear charge $+Ze$, $\langle V_{ee} \rangle(Z) = -(5Z/4)E_0$ is the value of the electron-electron repulsion term when recalculated with the wavefunction in Equation 13.2.26 [actually, all we need to do is to make the substitution $a_0 \rightarrow (2/Z)a_0$], and

$$\langle U \rangle(Z) = 2(Z-2) \left(\frac{e^2}{4\pi\epsilon_0} \right) \left\langle \frac{1}{r} \right\rangle. \quad (13.2.32)$$

Here, $\langle 1/r \rangle$ is the expectation value of $1/r$ calculated for a hydrogen atom with nuclear charge $+Ze$. It follows from Equation ([e9.74]) [with $n=1$, and making the substitution $a_0 \rightarrow a_0/Z$] that

$$\left\langle \frac{1}{r} \right\rangle = \frac{Z}{a_0}. \quad (13.2.33)$$

Hence,

$$\langle U \rangle(Z) = -4Z(Z-2)E_0, \quad (13.2.34)$$

because $E_0 = -e^2/(8\pi\epsilon_0 a_0)$. Collecting the various terms, our new expression for the expectation value of the Hamiltonian becomes

$$\langle H \rangle(Z) = \left[2Z^2 - \frac{5}{4}Z - 4Z(Z-2) \right] E_0 = \left(-2Z^2 + \frac{27}{4}Z \right) E_0. \quad (13.2.35)$$

The value of Z that minimizes this expression is the root of

$$\frac{d\langle H \rangle}{dZ} = \left(-4Z + \frac{27}{4} \right) E_0 = 0. \quad (13.2.36)$$

It follows that

$$Z = \frac{27}{16} = 1.69. \quad (13.2.37)$$

The fact that $Z < 2$ confirms our earlier conjecture that the electrons partially shield the nuclear charge from one another. Our new estimate for the ground-state energy of helium is

$$\langle H \rangle(1.69) = \frac{1}{2} \left(\frac{3}{2} \right)^6 E_0 = -77.5 \text{ eV}. \quad (13.2.38)$$

This is clearly an improvement on our previous estimate in Equation 13.2.25 (Recall that the correct result is -78.98 eV .)

Obviously, we could get even closer to the correct value of the helium ground-state energy by using a more complicated trial wavefunction with more adjustable parameters.

Note, finally, that because the two electrons in a helium atom are indistinguishable fermions, the overall wavefunction must be *anti-symmetric* with respect to exchange of particles. (See Chapter [smany].) Now, the overall wavefunction is the product of the spatial wavefunction and the spinor representing the spin-state. Our spatial wavefunction ([e14.44]) is obviously symmetric with

respect to exchange of particles. This means that the spinor must be anti-symmetric. It is clear, from Section [\[shalf\]](#), that if the spin-state of an $l = 0$ system consisting of two spin one-half particles (i.e., two electrons) is anti-symmetric with respect to interchange of particles then the system is in the so-called singlet state with overall spin zero. Hence, the ground-state of helium has overall electron spin zero.

Contributors and Attributions

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