On a scale of 0 to 10 in difficulty, the infinite square well is a 1. The one-dimensional harmonic oscillator is a 3. The hydrogen atom is an 8. And the helium atom is a 99.

But let’s take a crack at it anyway, and see how far we can get.

I’ll attack the problem by starting with the known solutions for the hydrogen atom, then introducing three changes, one at a time:

1. Increase the nuclear charge from $e$ to $2e$.

2. Introduce a second electron that’s also attracted to the nucleus, but neglect the repulsive force between the two electrons.

3. Finally, try to calculate the effects of the electron-electron repulsion.

### Increasing the nuclear charge

For a single electron in the vicinity of a nucleus containing $Z$ protons, the potential energy function becomes

$$ V(r) = -\frac{Ze^2}{4\pi\epsilon_0 r}. \quad (1) $$

Everything else in the Schrödinger equation is the same as for hydrogen, so there’s no need to solve it from scratch; we can simply modify the hydrogen solutions by slipping in a factor of $Z$ wherever $e^2$ appears. So the Bohr radius,

$$ a_0 = \frac{4\pi\epsilon_0 \hbar^2}{e^2 m} = \frac{4\pi\epsilon_0 h^2}{e^2 m} = 0.529 \times 10^{-10} \text{ m}, \quad (2) $$

gets divided by $Z$, meaning that all the wavefunctions get pulled in closer to the nucleus by a factor of $Z$. Meanwhile the hydrogen energy levels,

$$ E_n = -\frac{1}{2} \left( \frac{e^2}{4\pi\epsilon_0} \right)^2 \frac{m}{\hbar^2} \frac{1}{n^2} = -\frac{13.6 \text{ eV}}{n^2}, \quad (3) $$

get multiplied by a factor of $Z^2$, meaning that all the levels become much more negative as $Z$ increases.

We could simply modify our natural unit system to absorb these factors of $Z$, but nobody does that. We will continue to use atomic units, with distances in units of $a_0$ and energies in units of $E_h = 27.2 \text{ eV}$. In the formulas for the wavefunctions, we’ll need to replace every $a_0$ with $a_0/Z$ to transition from hydrogen to a heavier one-electron ion.

Helium, of course, has $Z = 2$, so for the He$^+$ ion, with only one electron, the wavefunctions are half as large as for hydrogen and the energies are four times as negative.
Adding a second electron

Now imagine that we start with a He\(^+\) ion and bring in a second electron, but magically turn off the repulsive force between the two electrons. Then each of the two electrons behaves more or less independently, feeling the same force from the nucleus and having the same energy levels and definite-energy wavefunctions.

I say “more or less,” because electrons are identical fermions, so even if they don’t exert any forces on each other, their combined wavefunction still needs to be antisymmetric under the hypothetical operation of interchanging them with each other. However, this combined wavefunction also includes their spin states. As we’ll study in a couple of weeks, the spin state alone, for a system of two spin-1/2 particles, can be either symmetric or antisymmetric. This means that the position-dependent part of the wavefunction can be, respectively, either antisymmetric or symmetric under interchange. The bottom line is that the antisymmetrization requirement doesn’t affect the number of available spatial wavefunctions.

Moreover, as you’ll see in a moment, all we’re really looking for here is a set of orthonormal basis functions to use in our subsequent calculations. For this purpose we don’t even need to use symmetric or antisymmetric wavefunctions; we can simply multiply a wavefunction for electron 1 by a wavefunction for electron 2. Our basis, therefore, looks something like this:

\[
\psi_{100}(r_1)\psi_{100}(r_2), \ \psi_{100}(r_1)\psi_{200}(r_2), \ \psi_{200}(r_1)\psi_{100}(r_2), \ \psi_{100}(r_1)\psi_{210}(r_2), \ldots, \tag{4}
\]

where the subscripts are the quantum numbers \(n, l, \) and \(m,\) respectively. (Remember that these \(\psi\) functions are all “squeezed” by a factor of 2 compared to those for hydrogen, as discussed above.) Still ignoring the repulsion between the two electrons, the energies of these wavefunctions are, in atomic units,

\[
E_{n_1, n_2} = -\frac{2}{n_1^2} - \frac{2}{n_2^2} = -4, -2.5, -2.5, -2.5, \ldots, \tag{5}
\]

where \(n_1\) and \(n_2\) are the principal quantum numbers associated with \(r_1\) and \(r_2,\) respectively. Note that, as with hydrogen, the difference in an electron’s energy between \(n = 1\) and \(n = 2\) is greater than the difference between \(n = 2\) and \(n = \infty;\) this means that if both electrons are in excited states, the atom has enough energy to ionize itself, ejecting one electron while the other drops to the ground state.

Electron-electron repulsion

The Hamiltonian for the hypothetical system I’ve just described, with two electrons but no repulsion between them, is (in atomic units)

\[
H_0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2}, \tag{6}
\]
where $\nabla_1$ is the $\nabla$ operator with derivatives taken with respect to $r_1$, and similarly for $\nabla_2$. To put in the electrostatic repulsion between the two electrons, we add one more term to the Hamiltonian:

$$\Delta V = + \frac{1}{|r_2 - r_1|}. \quad (7)$$

This simple-looking addition makes it impossible to find exact formulas for the eigenfunctions and eigenvalues. My approach, therefore, will be to construct the Hamiltonian matrix (or at least a significant part of it) in the basis of “unperturbed” two-particle wavefunctions described above, and then diagonalize this matrix to obtain the new energy levels and their associated eigenfunctions.

Notice that the basis functions (4) are already eigenfunctions of $H_0$, with the eigenvalues listed in equation 5. This means that the $H_0$ matrix is diagonal, with entries equal to the $H_0$ eigenvalues. Our only task, then, is to evaluate the matrix elements of $\Delta V$, so we can add this matrix onto $H_0$.

A typical matrix element of $\Delta V$ looks like this:

$$\int d^3r_1 \int d^3r_2 \psi^{*}_{n_{1}l_{1}m_{1}}(r_1) \psi^{*}_{n_{2}l_{2}m_{2}}(r_2) \frac{1}{|r_2 - r_1|} \psi_{n_{3}l_{3}m_{3}}(r_1) \psi_{n_{4}l_{4}m_{4}}(r_2). \quad (8)$$

Yep, it’s a six-dimensional integral. Unfortunately, you can’t just type such an expression into Mathematica and tell it to \texttt{NIntegrate}. We’ll have to do at least some of the integrals by hand.

I’ll simplify the problem enormously by restricting my attention to the $l = 0$ matrix elements. These are sufficient to obtain the helium states that have zero orbital angular momentum, including the ground state. (There are sophisticated tricks, involving spherical harmonics and angular momentum algebra, for handling the higher-$l$ states.) Each of the $l = 0$ wavefunctions consists of a radial wavefunction, $R_{nl}(r)$, multiplied by the trivial spherical harmonic $Y^0_0 = 1/\sqrt{4\pi}$. The only angular dependence in the integrand is then in $\Delta V$ itself, and this we can handle.

Taking $r_1$ to be temporarily fixed, we orient the $r_2$ coordinates with the $z_2$ axis pointing along $r_1$ (see Griffiths, Section 7.2, where there’s a figure). Then the integrand is independent of $\phi_2$, so the $\phi_2$ integral gives a trivial factor of $2\pi$, while (as Griffiths shows) the $\theta_2$ integral gives the nontrivial but delightfully simple result

$$\int_0^\pi \frac{\sin \theta_2}{|r_2 - r_1|} d\theta_2 = \frac{2}{r_\succ}, \quad (9)$$

where $r_\succ$ is the greater of $r_1$ and $r_2$. (The $\sin \theta_2$ in the numerator of the integrand comes from the measure of the integral in spherical coordinates.)

Now let’s do some mental cleanup. We can combine the 2 in the numerator of equation 9 with the $2\pi$ from the $\phi_2$ integral to cancel two of the factors of $1/\sqrt{4\pi}$ from the spherical harmonics. The $\theta_1$ and $\phi_1$ integrals give a trivial factor of $4\pi$ to cancel the other two spherical harmonics. The measures of the integrals also
contain two factors of \( r_1 \) and two factors of \( r_2 \), but we can absorb these into the radial wavefunctions to obtain the reduced radial wavefunctions, \( u_{nl}(r) \). Our generic \( l_1 = l_2 = 0 \) matrix element is therefore

\[
\Delta V_{n_1n_2n_3n_4} = \int dr_1 \int dr_2 u_{n_10}(r_1)u_{n_20}(r_2) \frac{1}{r_1} u_{n_30}(r_1)u_{n_40}(r_2). \quad (10)
\]

We’ve reduced a six-dimensional integral to a two-dimensional integral. What’s more, this two-dimensional integral can be done either analytically (see Griffiths for an example) or with \texttt{NIntegrate}.

In class I’ll show you some Mathematica code to evaluate these matrix elements and then construct a truncated Hamiltonian matrix from just the following basis states (listing \( n_1 \) and \( n_2 \), respectively, for each):

\[
1, 1 \quad 1, 2 \quad 2, 1 \quad 1, 3 \quad 3, 1 \quad 1, 4 \quad 4, 1
\]

(Notice that at least one of the electrons is always in the ground state, so none of these states have enough energy to self-ionize.) When we diagonalize this \( 7 \times 7 \) matrix, we’ll get a reasonably good approximation to the measured energies of the ground state and the two lowest excited states of helium. To put these results into context, please look at the energy level diagram in Section 5.2.1 of Griffiths.

This truncated-matrix approach to the helium atom, including the Mathematica code that I’ll show in class, is based on a recent article by Robert C. Massé and Thad G. Walker, “Accurate energies of the He atom with undergraduate quantum mechanics,” Am. J. Phys. 83 (8), 730–732 (2015).