Calculating helium atomic excited states in coordinate space

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Two coupled Schrödinger equations are used to calculate excited states of atomic helium. Using product state functions for the two-electron state, the shooting method is used to numerically determine the energies of the allowed singlet and triplet levels. The calculations agree well with the data, and the coordinate-space basis yields Schrödinger equations for helium that are familiar to students who have used similar methods for the hydrogen atom. © *2015 American Association of Physics Teachers.*
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I. INTRODUCTION

The helium atom played an important role in the development of atomic physics. Since it could not be treated by the Bohr–Sommerfeld method, the helium problem led to the development of modern quantum mechanics and especially to the treatment of identical particles. A historical review is given in Ref. [1]. Helium is particularly interesting because it is the simplest of the multi-electron atoms, and the effects of indistinguishable particles play an important role in the energy spectrum. For these reasons, the helium atom is an indispensible topic in the undergraduate physics curriculum and is covered in most quantum and some computational physics textbooks.[2–4] Unfortunately, solving for the energy levels of helium is significantly more difficult than for hydrogen, so approximation methods are used. Helium is often used as an example for introducing the variational principle and for applying perturbation methods.

Quantum textbooks usually limit the treatment of helium to analytic methods, in which hydrogen-like wave functions are used in perturbation and exchange integrals.[2] These calculations can be improved using numerical methods described in computational physics textbooks. For example, the ground-state energy of helium can be approximated using Monte Carlo methods[3] or using the Hartree–Fock self-consistent field approximation.[4] The literature also contains articles on the numerical treatment of helium. For the ground state, these include Hartree–Fock self-consistent field methods,[5,6] variational methods,[7] using hydrogen states as a basis,[8,9] and including angular correlations of the two electrons.[10] For the helium atomic excited states, there are articles that use a perturbation approach,[11] a variational method,[12] and a finite number of basis states.[13] In this article, we present a calculation, to supplement textbook treatments of atomic helium, that solves for the energies and eigenstates in a way that is similar to solving the hydrogen atom using the Schrödinger equation. We use neither perturbation nor variational methods for the excited states.

Schrödinger's equation for the hydrogen atom is obtained by casting the operator eigenvalue equation $\hat{H}|\Psi\rangle = E|\Psi\rangle$ in a coordinate-space basis, which produces a differential equation to be solved for E and $\Psi(\vec{r}) = \langle \vec{r}|\Psi\rangle$. We follow this same approach for the atomic states of helium. We limit the treatment to singly excited states ($1snl$), with one electron in the $1s$ level. In this case, both the screening and exchange potentials contain only one term (see Appendix B) and the calculation is much simpler than if both electrons have $l \neq 0$.

For the $1snl$ states, the eigenstates will be of the form $\Psi(\vec{r}_1, \vec{r}_2) \propto \psi_{1s}(r_1)\psi_{nl}(r_2) \pm \psi_{nl}(r_1)\psi_{1s}(r_2)$. We show in Appendix A how one obtains coupled Schrödinger equations from the operator eigenvalue equation. The coupled differential equations can be solved numerically, using the "shooting method," and the results match the data well.

In addition to using the same approach as for hydrogen, solving the helium atom in a coordinate-space basis has other advantages. Students can see how one obtains differential equations for identical particles from the operator eigenvalue equation. One does not use a specific form for the state functions, as is done with the variational approach. There are no free parameters in a trial wave function to vary. Although the solution is an approximation, one is not using perturbation theory. The approximation is not in solving the differential equations, but that the basis, although infinite, does not span the complete two-particle state space for identical particles. The students will also see the difficulties and limitations of directly solving coupled differential equations for the energies and state functions of multi-electron atoms. Finally, although the method uses an approximation, the results are quite accurate, within 0.04 eV, for the excited states.

In order to give the best overview of the calculation, we start with the differential equations and then discuss their numerical solution. In Appendix A, we derive the coupled differential equations—effective Schrödinger equations—from the operator eigenvalue equation $\hat{H}|\Psi\rangle = E|\Psi\rangle$. In Appendix B, we discuss how the screening and exchange potentials are obtained. In Appendix C, we show that the triplet s states can be determined using the approach presented here. The article closes with a review of the ground-state calculation and the results for the excited atomic states of helium.

II. THE SCHRÖDINGER EQUATIONS

We start with the nonrelativistic Hamiltonian for the helium atom

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} + \hat{V}_{N1} + \hat{V}_{N2} + \hat{V}_{12}, \tag{1}$$

where $\hat{V}_{N1}$ and $\hat{V}_{N2}$ are the Coulomb potential energy operators for each electron due to the nucleus, while $\hat{V}_{12}$ is the potential energy operator representing the Coulomb interaction of the two electrons with each other. For m we use the

electron's mass, as is done in undergraduate textbooks for the treatment of the helium atom.[2–4] The correction due to the motion of the nucleus, a three-body reduced mass problem, is difficult to include. An estimate for this correction of the ground-state energy of helium is[14] 0.00014 times the ground-state energy. If this fractional error were applicable to the excited states, a ≈ 0.008-eV shift would result. We are also neglecting any terms in $\hat{H}$ that depend directly on spin. The largest term would be the spin-orbit interaction. From Ref. 15, the spin-orbit splitting for the 2p excited state of helium is ≈10^{-4} eV.

The goal is to find the eigenvalues E of $\hat{H}$

$$\hat{H}|\Psi_{12}\rangle = E|\Psi_{12}\rangle, \tag{2}$$

where $|\Psi_{12}\rangle$ is the two-electron state. Because the two electrons are identical fermions, $|\Psi_{12}\rangle$ must change sign upon particle exchange. Nonrelativistically, the space and spin parts of the state can be separated. The spins can combine to be $S = 0$ (singlet), which changes sign under particle exchange, or $S = 1$ (triplet), which is unchanged under particle exchange.

Consider first the ground state. Since we are interested in solving a differential equation, i.e., the Schrödinger equation, for the allowed energies E, we use a coordinate space basis. As a simple ansatz that satisfies the requirements of identical particles, we choose for the ground state

$$\langle \vec{r}_1 \vec{r}_2 | \Psi_{12} \rangle = R_{1s}(r_1) Y_{00}(\Omega_1) R_{1s}(r_2) Y_{00}(\Omega_2), \tag{3}$$

where $R_{1s}(r_i)$ is the radial function and $Y_{00}(\Omega_i)$ is the spherical harmonic for electron i. The function R_{1s} is the same function for each electron, and is initially unknown. We note that the ground-state function is symmetric upon particle exchange, since the ground state has $S = 0$. After comparing with the data, we will discuss the limitations of using this form.

In Appendix A, we show how to obtain differential equations, Schrödinger equations, from Eq. (2). By operating on the left with the bra $\langle r_1|\langle\psi_{1s}|_2$ times $Y_{00}(\Omega_1)$ and integrating over Ω_1, we obtain the following differential equation for $u_{1s}(r) \equiv rR_{1s}(r)$:

$$-\frac{\hbar^2}{2m}\frac{d^2u_{1s}(r)}{dr^2} - \frac{2e^2}{r}u_{1s}(r) + V_{C1s}(r)u_{1s}(r) = E'u_{1s}(r). \tag{4}$$

The term $-2e^2/r$ is the electrostatic Coulomb potential due to the nucleus, while $V_{C1s}(r)$ is the repulsive Coulomb screening potential due to the other electron. This function depends on $u_{1s}(r)$, and is in this case the potential due to a spherically symmetric charge distribution with density $R_{1s}^2(r)$. We describe how to solve for $u_{1s}(r)$ and E' in a self-consistent way in Sec. III.

For singly excited states where one electron is in the lowest $l = 0$ state and the other electron in the nl state, we choose the form

$$\langle \vec{r}_1 \vec{r}_2 | \Psi_{12} \rangle = \frac{1}{\sqrt{2}} \big[R_{1s}(r_1) Y_{00}(\Omega_1) R_{nl}(r_2) Y_{lm}(\Omega_2)$$
$$\pm R_{nl}(r_1) Y_{lm}(\Omega_1) R_{1s}(r_2) Y_{00}(\Omega_2) \big], \tag{5}$$

with the + for the singlet and the – for the triplet. For these excited states, there are two radial functions to be

determined, $R_{1s}(r)$ and $R_{nl}(r)$. By operating on the left of both sides of Eq. (2) with the appropriate bras (see Appendix A), we obtain differential equations that are effective Schrödinger equations for $u_{1s}(r)$ and $u_{nl}(r)$

$$-\frac{\hbar^2}{2m}\frac{d^2u_{1s}(r)}{dr^2} - \frac{2e^2}{r}u_{1s}(r) + V_{Cnl}(r)u_{1s}(r)$$
$$\pm V_x(r)u_{nl}(r) = E'u_{1s}(r), \tag{6}$$

$$-\frac{\hbar^2}{2m}\left(\frac{d^2u_{nl}(r)}{dr^2} - \frac{l(l+1)}{r^2}u_{nl}(r)\right) - \frac{2e^2}{r}u_{nl}(r)$$
$$+ V_{C1s}(r)u_{nl}(r) \pm V_x(r)u_{1s}(r) = E''u_{nl}(r). \tag{7}$$

The terms $-2e^2/r$ are the electrostatic Coulomb potentials for each electron due to the nucleus, while $V_{C1s}(r)$ and $V_{Cnl}(r)$ are the repulsive Coulomb screening potentials due to the other electron. The function $V_{C1s}(r)$ depends on $u_{1s}(r)$ and is the potential due to a spherically symmetric charge distribution with density $R_{1s}^2(r)$. The function $V_{Cnl}(r)$ depends on $u_{nl}(r)$ and is due to a spherically symmetric charge distribution with density $R_{nl}^2(r)$.

The function $V_x(r)$ in Eqs. (6) and (7) is a "Coulomb exchange" potential. In this case, as shown in Appendix B, it is the potential due to a charge distribution equal to $R_{1s}(r)R_{nl}(r)Y_{lm}(\Omega)$. Without the term $V_x(r)$, the two differential equations would separate, with Eq. (6) containing only $u_{1s}(r)$ and Eq. (7) containing only $u_{nl}(r)$. The potential $V_x(r)$ couples the two equations, similar to the way that a "mixing potential" is used in a coupled-channels calculation in atomic and nuclear physics to represent the interaction of the particles or states with each other.[17] Here, however, even without $V_x(r)$ the nl state and 1s state affect each other via the Coulomb screening potentials. The $V_x(r)$ term is a direct coupling of the equations as a result of the two particles being identical.

We note that both Coulomb screening potentials, $V_{C1s}(r)$ and $V_{Cnl}(r)$, for the singly excited states are spherically symmetric and can be relatively easily determined using Gauss's law. The exchange potential V_x can be determined from Poisson's equation. The application of the method used here for atoms with $Z > 2$ electrons would be difficult. One would have Z coupled differential equations, with $Z - 1$ Coulomb screening and exchange potentials in each equation. For $Z > 2$, a Hartree–Fock approach would be a better choice.

III. NUMERICAL METHODS

We now discuss how the Schrödinger equations (4), (6), and (7) can be solved numerically. There are two aspects to solving the equations: the numerical solution of the equation, for which we use a shooting method, and the self-consistency of the various potential functions with the state functions. We begin with the ground state, then describe the extension to the excited states.

For the ground state, we need to solve Eq. (4), which we rewrite dropping the subscripts on u for brevity

$$-\frac{\hbar^2}{2m}\frac{d^2u(r)}{dr^2} - \frac{2e^2}{r}u(r) + V_{C1s}(r)u(r) = E'u(r). \tag{8}$$

The boundary conditions on $u(r)$, $u(0) = 0$ and $u(r \to \infty) \to 0$, can only be satisfied for certain values of E', which are

related to the allowed bound-state energies of the system. The potential $V_{C1s}(r)$ depends on $u(r)$ (see Appendix B).

We solve Eq. (8) numerically using the "shooting method" as described in Ref. 16, which we summarize. The shooting method is used to solve boundary value problems by adjusting the unknown parameter to match the boundary values. In our case, the boundary values are $u(r) = 0$ and $u(r \rightarrow \infty) \rightarrow 0$. The radial coordinate is made discrete with a step size Δ. The variable r, $u(r)$, and the potentials become arrays: $r \rightarrow r(i) = i\Delta$, $u(r) \rightarrow u(r(i)) \rightarrow u(i)$, and $V_{C1s}(r) \rightarrow V_{C1s}(i)$. We use a finite difference method for the second derivative of $u(r)$

$$\frac{d^2 u(r)}{dr^2} \rightarrow \frac{u(i+1) + u(i-1) - 2u(i)}{\Delta^2}. \quad (9)$$

After substituting this expression into Eq. (8), one obtains a discrete version of the differential equation

$$u(i+1) = 2u(i) - u(i-1)$$
$$+ \frac{2m\Delta^2}{\hbar^2}\left(-\frac{2e^2}{r(i)} + V_{C1s}(i) - E'\right)u(i). \quad (10)$$

In the shooting method, one starts with a trial energy E', which lies below the expected value. As a start we assign $u(0) = 0$ and $u(1) = 1.0$. After the first iteration of Eq. (10), we assign $u(0) = 0$ and $u(1)$ to be the value it had in the previous iteration after normalization. From Eq. (10), $u(i+1)$ is determined from $u(i)$, $u(i-1)$, and values of the potentials at i. We use Eq. (10) to iterate $u(i)$ out to some large value of i, called $i_{\max}$. We assign $u(i_{\max})$ the value t_0. Next, the trial energy is increased by an amount $\delta E'$ and the process is repeated. The function $u(i_{\max})$ will have a different value, which we call t_1. If t_1 and t_0 have the same sign, then the trial energy is changed again by an amount $\delta E'$, $t_1 \rightarrow t_0$, and the process is repeated. Once t_1 and t_0 have opposite signs, then the wave function has changed sign at $r = i_{\max}\Delta$, and the trial energy has passed over the bound-state energy. When t_1 and t_0 have opposite signs, the energy step is reversed and halved, $\delta E' \rightarrow -\delta E'/2$, $t_1 \rightarrow t_0$, and the process is repeated to the desired accuracy. In our calculations, we choose $\Delta = 0.001$ Å and $i_{\max} = 15000$. The code is checked for accuracy by requiring the numerical energies E' obtained without V_{C1s} to agree, to six significant figures, with the helium ion energies $54.4178/n^2$ eV. All variables are set to double precision.

We start by taking the electrostatic potential $V_{C1s}(i)$ to be that produced by an electron in the $1s$ state of a singly ionized helium atom. After Eq. (10) is solved, the screening potential $V_{C1s}(i)$ is updated with the new function $u(i)$. For the update, $V_{C1s}(i)$ is calculated with $u(i)$ normalized to one: $\sum_i u(i)^2 \Delta = 1$. If the energy E' is not *exactly* equal to the correct bound-state energy, the function $u(i)$ will increase without limit as $i \rightarrow \infty$. To obtain the normalized wave function, we let i start at $i_{\max}$ and decrease i until $|u(i)|$ is a minimum. Once this value of $i = i_{\text{match}}$ is found, then we set $u(i)$ equal to zero for values of $i > i_{\text{match}}$. The function $u(i)$ is then normalized such that $\sum_i u(i)^2 \Delta = 1$. For example, in the $1s2s$ triplet calculation, $i_{\text{match}} \approx 5000$, which corresponds to 5 Å. The value of $u_{1s}(5000)$ is around 10^{-8} of the maximum value of $u_{1s}(r)$ near 0.3 Å.

With the screening potential updated with the new $u(i)$, Eq. (10) is solved for new values of E' and $u(i)$. The next iteration updates the screening potential $V_{C1s}(i)$, and the process is repeated until self-consistency is accomplished. A flow diagram for the ground-state calculation is shown in Fig. 1. Self-consistency means that $u(i)$ is a solution of Eq. (10) for a screening potential determined from a charge density $\rho(i) = eu^2(i)/r(i)^2$, where $\sum_i u(i)^2 \Delta = 1$. Self-consistency is reached after less than 20 iterations for the ground state. The computer code we used for the ground-state calculation is provided in the supplementary material of this paper.[18]

For the excited states, the shooting method can also be used for the coupled Schrödinger equations, Eqs. (6) and (7). Following the same procedure as with the ground state, the radial coordinate is made discrete with step size Δ. Using Eq. (9) for the second derivatives, one obtains discrete versions of Eqs. (6) and (7)

$$u_{1s}(i+1) = 2u_{1s}(i) - u_{1s}(i-1)$$
$$+ \frac{2m\Delta^2}{\hbar^2}\left(-\frac{2e^2}{r(i)} + V_{Cnl}(i) - E'\right)u_{1s}(i)$$
$$\pm \frac{2m\Delta^2}{\hbar^2}V_x(i)u_{nl}(i) \quad (11)$$

and

$$u_{nl}(i+1) = 2u_{nl}(i) - u_{nl}(i-1) + \Delta^2\frac{l(l+1)}{r(i)^2}u_{nl}(i)$$
$$+ \frac{2m\Delta^2}{\hbar^2}\left(-\frac{2e^2}{r(i)} + V_{C1s}(i) - E''\right)u_{nl}(i)$$
$$\pm \frac{2m\Delta^2}{\hbar^2}V_x u_{1s}(i), \quad (12)$$

where the $+$ is for the singlet and the $-$ for the triplet states.

We start by taking $u_{1s}(i)$ to be the $1s$ wave function for singly ionized helium, and $u_{nl}(i)$ to be the nl wave function of hydrogen. The potentials $V_x(i)$ and $V_{Cnl}(i)$ are determined from these trial functions. Then the procedure shown in Fig. 2 is carried out until self-consistency is obtained.

We solve Eq. (11) for the lowest bound state of energy E', and the function $u_{1s}(i)$. The new $u_{1s}(i)$ is used to update V_{C1s} and V_x for Eq. (12). Then we solve Eq. (12) for the lowest bound-state energy E'' and an updated $u_{nl}(i)$. The new u_{nl} is used to update V_{Cnl} and V_x for Eq. (11). The process is repeated until $u_{1s}(i)$ and $u_{nl}(i)$ do not change, and the equations are self-consistent. Thus, the functions $u_{1s}(i)$ and $u_{nl}(i)$ are solutions to the coupled equations with screening and exchange potentials calculated from the same $u_{1s}(i)$ and $u_{nl}(i)$. The computer codes we used for the excited state calculations can be found in the supplementary material.[18]
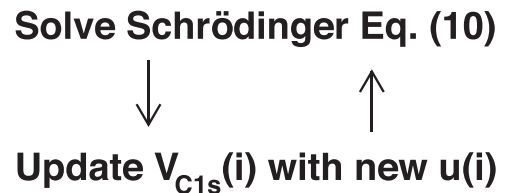
Solve Schrödinger Eq. (10)

Update $V_{C1s}(i)$ with new u(i)

Fig. 1. Flow diagram for the ground-state calculation. After Eq. (10) is solved for E' and $u(i)$, $V_{C1s}(i)$ is updated with the new $u(i)$. The process is repeated until self-consistency is reached.

The shooting method is a relatively easy way to solve for the bound-state energies and wave functions. Other techniques for numerically solving differential equations can be used. We have had success with the shooting method approach in our computational physics classes. The method is straightforward, and the students can visualize how the wave function approaches zero at the special bound-state energies. We discuss the results in Secs. IV–VIII.

IV. HELIUM GROUND STATE

The helium ground-state calculation is a good example to demonstrate a self-consistent potential calculation. Using Eq. (10), self-consistency is reached after less than 20 iterations with the following results: $E' = 24.98$ eV, $A = 91.82$ eV, and $B = -38.93$ eV, which gives a ground-state binding energy equal to $E = E' + A + B = 77.87$ eV.[18] This value of E is to be compared to the experimental value of 79.005 eV. This self-consistent potential result for the helium ground state is well known.

It is instructive to consider why the theoretical calculation does not agree with experiment. The numerical solution of Eq. (10) can be made more accurate by making Δ smaller, but this will only improve the number of significant figures in the calculation; it will not close the discrepancy between the calculation and experiment. Since we did not pick any particular form for the wave function $u(r) = rR(r)$ as is often done using variational methods, we can't improve our results by changing the shape for $R(r)$. We have not made any approximations in solving the equation. However, although our form for $\Psi(\vec{r}_1, \vec{r}_2)$ in Eq. (3) is of infinite dimension and symmetric in $\vec{r}_1$ and $\vec{r}_2$, it does not span the complete space of possible wave functions for the indistinguishable electrons. Hence, our result will be higher in energy than the energy obtained using a complete basis. A more complete basis will include angular correlations, where the (un-normalized) form of the wave function is

$$\langle \vec{r}_1 \vec{r}_2 | \Psi_{12} \rangle = R_0(r_1)R_0(r_2) + \sum_l a_l R_l(r_1)R_l(r_2)$$

$$\times \left(\sum_{m=-l}^{l} \langle 00|lml-m \rangle Y_{lm}(\Omega_1)Y_{l-m}(\Omega_2) \right)$$

$$= R_0(r_1)R_0(r_2) + \sum_l a_l R_l(r_1)R_l(r_2)$$

$$\times P_l(\cos(\hat{r}_1 \cdot \hat{r}_2)). \quad (13)$$

Solve Schrödinger Eq. (11)

Update $V_x(i)$ and $V_{C1s}(i)$ with new $u_{1s}(i)$ **Update $V_x(i)$ and $V_{Cnl}(i)$ with new $u_{nl}(i)$**
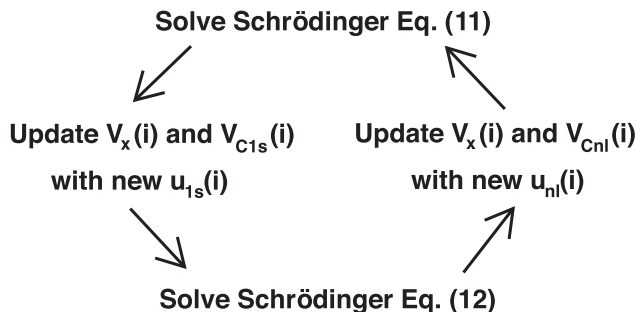
Solve Schrödinger Eq. (12)

Fig. 2. Flow diagram for the excited states. After Eq. (11) is solved for E' and $u_{1s}(i)$, $V_x(i)$ and $V_{C1s}(i)$ are updated with the new $u_{1s}(i)$. After Eq. (12) is solved for E'' and $u_{nl}(i)$, $V_x(i)$ and $V_{Cnl}(i)$ are updated with the new $u_{nl}(i)$. The process is repeated until self-consistency is reached.

The function on the right is symmetric under exchange of $\vec{r}_1$ and $\vec{r}_2$, and is an eigenstate of $\hat{L}^2$ with eigenvalue zero. This is a difficult extension, and perhaps too difficult for the undergraduate classroom. We have included the $l = 1$ term in the sum with the result that $E = 78.54$ eV. As we shall see, excluding angular correlations for the excited states yields results that are slightly above experiment.

In Table I, we list the results for the ground and excited states. The energy that is being calculated is the difference in energy between the helium atomic states and the helium nucleus plus two free electrons. All the experimental data in Table I are found in Ref. 15. The ionization energy of the helium ground state is 24.5874 eV, which is added to the energy of 54.4178 eV needed to remove the single electron from the helium ion. The ground-state energy becomes 79.0052 eV $\approx$ 79.005 eV as listed in the table. In the first column, for comparison, we list the sum of the energies of a single electron bound to a helium nucleus, 54.4178 eV, plus a single electron bound to the helium nucleus that is completely screened by the other electron, $(54.4178/2^2)/n^2 \approx 13.6044/n^2$, in eV.

V. EXCITED p STATES

The results for the $1s2p$ and $1s3p$ states[18] are shown in Table I. We list the contributions from the different parts of Eqs. (11) and (12). The initial column is the energy of the "simple screening" state without any screening for the $1s$ electron and complete screening for the $2p$ electron. The next column lists the results of solving Eqs. (11) and (12) without the exchange potential. The last column is the complete calculation, which can be compared with the experimental result in the last column. We estimate the numerical accuracy of the $1s2p$ singlet result to be ± 0.005 eV and the $1s2p$ triplet result to be ± 0.01 eV, which is the difference between the calculations for E using $E = E'' + A' + B'$ and $E = E' + A + B$ (see Appendix A). The accuracies for the $1s3p$ results are 0.003 eV for the singlet and 0.007 eV for the triplet.

Some results for the p-state energy levels are worth noting. The four p-state calculations agree quite well with

Table I. Experimental and calculated values for the energy levels of the helium atom. All values are in units of—eV. The experimental values are from Ref. 15. The energies listed in the "with screening" column are calculated without the exchange potential in Eqs. (11) and (12). The energies listed in the "+ exchange term" column are the complete calculation of Eqs. (11) and (12).

Level	$54.4178 + 13.6044/n^2$	With screening	+ exchange term	Experiment
Ground state	68.022	77.87	–	79.005
2s(triplet)	57.82	58.58	59.16	59.19
2s(singlet)	57.82	58.58	–	58.39
2p(triplet)	57.82	57.85	58.00	58.04
2p(singlet)	57.82	57.85	57.75	57.79
3s(triplet)	55.929	56.137	56.280	56.287
3s(singlet)	55.929	56.137	–	56.085
3p(triplet)	55.929	55.940	55.988	55.998
3p(singlet)	55.929	55.940	55.908	55.918
3d(triplet)	55.929	55.930	55.930	55.931
3d(singlet)	55.929	55.930	55.930	55.931

experiment. Also, in both cases, the singlet-triplet splitting matches the data to the accuracy listed. The singlet-triplet splitting for the $1s2p$ state can be compared with data from a student laboratory experiment.[19] It is interesting to note that the exchange potential affects the singlet state different than the triplet state. In the case of the $2p$ states, the binding energy of the triplet is increased by 0.15 eV whereas for the singlet state it is decreased by 0.10 eV. In first order perturbation theory, the correction treated in textbooks, the increase for the triplet state equals the decrease for the singlet state. For the $2p$ (and $3p$) singlet states, the amount of Coulomb screening energy is approximately equal and opposite to the exchange energy. The result is that simple screening for these states agrees quite well with the data. A diagram of the results in Table I for the $n = 2$ level is shown in Fig. 3.

VI. EXCITED d STATES

The results for the $3d$ excited states[18] are listed in Table I. It is seen that the exchange energy is small and that simple screening gives approximately the same energy shift as the complete screening calculation. Thus, for the $1s3d$ states, singlet-triplet splitting is very small and simple screening matches the data quite well. We estimate the numerical accuracy of the $1s3d$ results to be ± 0.0007 eV, which is the difference between the calculations for E using $E = E'' + A' + B'$ and $E = E' + A + B$ (see Appendix A). For these states, the outer electron does not significantly screen the inner one, and the inner electron almost completely screens the nucleus for the outer one. This property for the excited states $1snd$, where $n \geq 3$, assists in the analysis of the helium spectroscopic data.[19]

VII. EXCITED s STATES

One would like to apply the same method for the s-wave excited states as was done with the p-wave and d-wave states. Following the p and d excited states, the simplest ansatz for the $1sns$ state, where $n \geq 2$, is

$$\langle \vec{r}_1 \vec{r}_2 | \Psi_{12} \rangle = \frac{1}{\sqrt{2}} \left(R_{1s}(r_1) R_{ns}(r_2) \pm R_{1s}(r_2) R_{ns}(r_1) \right). \quad (14)$$

As with the excited p and d states, this form for Ψ can be substituted into the Hamiltonian eigenvalue equation.

However, a problem arises in that the two functions R_{1s} and R_{ns} are not orthogonal in general. In the p-wave case, R_{1s} and $R_{np}Y_{1m}$ were orthogonal due to the angular integral. In the s-wave case, the two electrons have the same angular dependence. The integral $\int R_{1s}(r) R_{ns}(r) r^2 \, dr$ is not necessarily zero. If R_{1s} and R_{ns} are not orthogonal, then there will be a large number of cross terms in the differential equations, which makes the calculation very difficult. All is not lost, however, because for the triplet case the radial wave functions turn out to be orthogonal (see Appendix C). In the case of the triplet $1sns$ states the cross terms vanish, and one is left with two solvable equations containing $R_{1s}(r)$ and $R_{ns}(r)$

$$-\frac{\hbar^2}{2m} \frac{d^2 u_{1s}(r)}{dr^2} - \frac{2e^2}{r} u_{1s}(r) + V_{Cns}(r) u_{1s}(r)$$
$$- V_x(r) u_{ns}(r) = E' u_{1s}(r), \quad (15)$$

$$-\frac{\hbar^2}{2m} \frac{d^2 u_{ns}(r)}{dr^2} - \frac{2e^2}{r} u_{ns}(r) + V_{C1s}(r) u_{ns}(r)$$
$$- V_x(r) u_{1s}(r) = E'' u_{ns}(r). \quad (16)$$

Note that only the $-V_x$ term enters the equations.

In some ways, the triplet s-wave excited states are easier to calculate than the p- and d-wave excited states. For the s-wave excited states, both the screening and exchange potentials are $L = 0$ spherically symmetric charge densities, and therefore quite easy to determine from the electron wave functions. Gauss's law can be used to determine the potentials V_{C1s}, V_{Cns}, and V_x. Also, the $l(l+1)/r^2$ piece is absent in the equation for u_{ns}. The screening and exchange energies are the largest of those for the excited states, and hence the agreement with experiment is all the more convincing of the effects of indistinguishable particles. The $1s2s$ energy agrees to within 0.03 eV and the $1s3s$ to within 0.01 eV with the triplet data.[18] We estimate the numerical accuracy of the $1s2s$ triplet state to be ± 0.003 eV and of the $1s3s$ triplet state to be ± 0.0009 eV, based on the difference between the calculations for E using $E = E'' + A' + B'$ and $E = E' + A + B$ discussed in Appendix A.

VIII. SUMMARY

Calculating excited states of atomic helium using coupled Schrödinger equations is an interesting exercise for undergraduate physics students and can supplement textbook
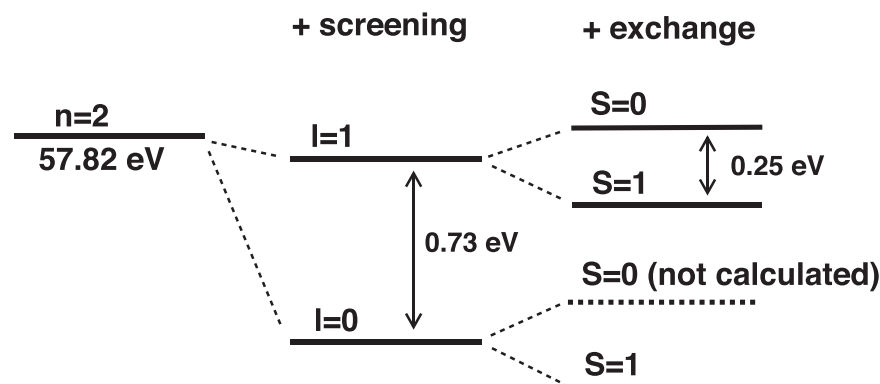

Fig. 3. Diagram of the results in Table I for the $n = 2$ level. If the interaction between the two electrons is neglected, all the $n = 2$ levels are degenerate with a binding energy of 57.82 eV. Including the Coulomb interaction of the two electrons with each other leads to a splitting of the $l = 1$ and $l = 0$ states, which we calculate to be 0.73 eV. Including the effect of indistinguishable particles splits the singlet and triplet states, by an amount that we calculate for the $2p$ level to be 0.25 eV.

analyses. This approach is appealing because it builds on students' experience with the hydrogen atom, and because the main approximation is that the state space is not the complete space for identical particles. The simplest states to apply this method to are the $1sns$ excited triplet states, since the wave functions are spherically symmetric and one can use Gauss's law to find the exchange potential.

APPENDIX A: SCHRÖDINGER EQUATIONS FOR HELIUM

The atomic states are solutions to $\hat{H}|\Psi_{12}\rangle = E|\Psi_{12}\rangle$, where

$$\hat{H} = \frac{\hat{p}_1^2}{2m} + \frac{\hat{p}_2^2}{2m} + \hat{V}_{N1} + \hat{V}_{N2} + \hat{V}_{12} \tag{A1}$$

is the nonrelativistic Hamiltonian operator for the two electrons, and $|\Psi_{12}\rangle$ is the two electron state. The operators $\hat{V}_{N1}$ and $\hat{V}_{N2}$ are the Coulomb potential energy operators for each electron due to the nucleus, while $\hat{V}_{12}$ is the Coulomb potential energy operator for the interaction between the two electrons. We are neglecting any terms in $\hat{H}$ that depend directly on spin.

In order to obtain the Schrödinger differential equation(s) from the operator equation, we start with the ground state of helium. One needs to use a coordinate space basis to cast the operator equation into a spatial differential equation. For a start, we choose $|\Psi_{12}\rangle = |\psi_{1s}\rangle_1|\psi_{1s}\rangle_2|S = 0\rangle_{12}$, since the ground state has spin zero. The spin state $|S = 0\rangle_{12}$ changes sign upon particle exchange, and the product $|\psi_{1s}\rangle_1|\psi_{1s}\rangle_2$ is the simplest choice that is symmetric upon particle exchange. In coordinate space, we have for this choice

$$\langle\vec{r}_1\vec{r}_2|\Psi_{12}\rangle = \langle\vec{r}_1|\psi_{1s}\rangle_1\langle\vec{r}_2|\psi_{1s}\rangle_2$$
$$= R_{1s}(r_1)Y_{00}(\Omega_1)R_{1s}(r_2)Y_{00}(\Omega_2). \tag{A2}$$

We first apply the bra $\langle\vec{r}_1|\langle\psi_{1s}|_2$ to both sides of Eq. (A1). Then, by multiplying by $Y_{00}(\Omega_1)$ and integrating over Ω_1 on both sides we can project out the radial function $R_{1s}(r_1)$. For the term on the right, we have

$$\int\langle\vec{r}_1|\langle\psi_{1s}|_2 E|\Psi_{12}\rangle Y_{00}(\Omega_1)d\Omega_1 = ER_{1s}(r_1). \tag{A3}$$

The results for each term on the left are as follows:

$$\int\langle\vec{r}_1|\langle\psi_{1s}|_2 \frac{\hat{p}_1^2}{2m}|\Psi_{12}\rangle Y_{00}(\Omega_1)d\Omega_1$$
$$= -\frac{\hbar^2}{2m}\int\nabla_1^2(R_{1s}(r_1)Y_{00}(\Omega_1)d\Omega_1$$
$$= -\frac{\hbar^2}{2m}\frac{1}{r_1^2}\frac{d}{dr_1}\left(r_1^2\frac{dR_{1s}(r_1)}{dr_1}\right), \tag{A4}$$

$$\int\langle\vec{r}_1|\langle\psi_{1s}|_2 \frac{\hat{p}_2^2}{2m}|\Psi_{12}\rangle Y_{00}(\Omega_1)d\Omega_1$$
$$= \langle\psi_{1s}|\frac{\hat{p}^2}{2m}|\psi_{1s}\rangle R_{1s}(r_1) \equiv AR_{1s}(r_1), \tag{A5}$$

$$\int\langle\vec{r}_1|\langle\psi_{1s}|_2 \hat{V}_{N1}|\Psi_{12}\rangle Y_{00}(\Omega_1)d\Omega_1 = -\frac{2e^2}{r_1}R_{1s}(r_1), \tag{A6}$$

$$\int\langle\vec{r}_1|\langle\psi_{1s}|_2 \hat{V}_{N2}|\Psi_{12}\rangle Y_{00}(\Omega_1)d\Omega_1$$
$$= -\langle\psi_{1s}|\frac{2e^2}{r}|\psi_{1s}\rangle R_{1s}(r_1) \equiv BR_{1s}(r_1), \tag{A7}$$

$$\int\langle\vec{r}_1|\langle\psi_{1s}|_2 \hat{V}_{12}|\Psi_{12}\rangle Y_{00}(\Omega_1)d\Omega_1$$
$$= \int e^2 Y_{00}^*(\Omega_2)\frac{R_{1s}^*(r_2)R_{1s}(r_2)}{|\vec{r}_1 - \vec{r}_2|}Y_{00}(\Omega_2)Y_{00}(\Omega_1)$$
$$\times d\Omega_1 d\Omega_2 r_2^2 dr_2 R_{1s}(r_1) \equiv V_{C1s}(r_1)R_{1s}(r_1). \tag{A8}$$

Substituting these terms into the Hamiltonian eigenvalue equation (A1) yields the following Schrödinger equation:

$$-\frac{\hbar^2}{2m}\frac{1}{r_1^2}\frac{d}{dr_1}\left(r_1^2\frac{dR_{1s}(r_1)}{dr_1}\right) - \frac{2e^2}{r_1}R_{1s}(r_1)$$
$$+ V_{C1s}(r_1)R_{1s}(r_1) = (E - A - B)R_{1s}(r_1), \tag{A9}$$

where A and B are defined in the previous equations. The quantity A is the expectation value of kinetic energy, and B is the expectation value of the nucleus-electron Coulomb energy for one of the $1s$ electrons.

It is convenient to use the function $u_{1s}(r_1) \equiv r_1 R_{1s}(r_1)$. For brevity, we write r_1 as simply r, and the Schrödinger equation becomes[16]

$$-\frac{\hbar^2}{2m}\frac{d^2u_{1s}(r)}{dr^2} - \frac{2e^2}{r}u_{1s}(r) + V_{C1s}(r)u_{1s}(r) = E'u_{1s}(r), \tag{A10}$$

where $E' \equiv E - A - B$. In terms of u_{1s}, A and B are simply

$$A = -\frac{\hbar^2}{2m}\int u_{1s}(r')\frac{d^2u_{1s}(r')}{dr'^2}\,dr' \tag{A11}$$

and

$$B = -2e^2\int\frac{u_{1s}^2(r')}{r'}\,dr', \tag{A12}$$

since $u_{1s}(r)$ is real. The potential $V_{C1s}(r)$ is the average electrostatic potential due to the other electron, and we discuss how to obtain it in Appendix B. For the ground state, $V_{C1s}(r)$ is just the electrostatic potential due to a spherical charge distribution with charge density $\rho(r) = R^2(r)/(4\pi) = u^2(r)/(4\pi r^2)$.

Next, we derive the coupled Schrödinger equations for the excited nl states. For these excited states, one electron is in the $1s$ state, and one electron is in the nl state. Since the electrons are in different spatial states, their spins can combine to be spin zero, $|S = 0\rangle_{12}$, or spin one, $|S = 1\rangle_{12}$. The spin-zero combination changes sign upon particle exchange, and the spin-one combination does not.

For simplicity, we take the following forms for the excited singlet and triplet states:

$$|\Psi_{12}\rangle = \frac{1}{\sqrt{2}}\left(|\psi_{1s}\rangle_1|\psi_{nl}\rangle_2 + |\psi_{nl}\rangle_1|\psi_{1s}\rangle_2\right)|S = 0\rangle_{12}, \tag{A13}$$

$$|\Psi_{12}\rangle = \frac{1}{\sqrt{2}}\left(|\psi_{1s}\rangle_1|\psi_{nl}\rangle_2 - |\psi_{nl}\rangle_1|\psi_{1s}\rangle_2\right)|S = 1\rangle_{12}, \tag{A14}$$

where both change sign under particle exchange. The state $|\psi_{1s}\rangle$ is an eigenstate of $\hat{L}^2$ with eigenvalue zero, and $|\psi_{nl}\rangle$ is an eigenstate of $\hat{L}^2$ with eigenvalue $\hbar^2 l(l+1)$. Thus, $\langle\psi_{1s}|\psi_{nl}\rangle$ equals 0 if $l \neq 0$. We discuss the excited s states in Appendix C. As with the ground state, we will be working in coordinate space to cast the eigenvalue problem into a differential equation. In coordinate space, we have for this choice

$$\sqrt{2}\langle\vec{r}_1\vec{r}_2|\Psi_{12}\rangle = R_{1s}(r_1)Y_{00}(\Omega_1)R_{nl}(r_2)Y_{lm}(\Omega_2)$$
$$\pm R_{1s}(r_2)Y_{00}(\Omega_2)R_{nl}(r_1)Y_{lm}(\Omega_1). \quad (A15)$$

There are two spatial functions, $R_{1s}(r)$ and $R_{nl}(r)$, to be determined. We can produce a differential equation for each function by taking the inner product of each side of Eq. (A1) with the appropriate bra. The differential equation for the 1s radial function, $R_{1s}(r)$, is obtained in a similar way as with the ground state. First, operate on both the right and left sides of Eq. (A1) with the bra $\sqrt{2}\langle\vec{r}_1|\langle\psi_{nl}|_2$. Then, multiply both sides by $Y_{00}(\Omega_1)$ and integrate over Ω_1 to project out $R_{1s}(r_1)$. For the right side of Eq. (A1), we have

$$\sqrt{2}\int\langle\vec{r}_1|\langle\psi_{nl}|_2 E|\Psi_{12}\rangle Y_{00}(\Omega_1)\,d\Omega_1 = ER_{1s}(r_1). \quad (A16)$$

Since $\langle\psi_{nl}|\psi_{1s}\rangle = 0$ for $l \neq 0$ and $\langle\psi_{nl}|\psi_{nl}\rangle = 1$, we have $\langle\psi_{nl}|_2 \Psi_{12}\rangle = (1/\sqrt{2})|\psi_{1s}\rangle_1$ yielding the simple result on the right side.

Multiplying by $Y_{00}(\Omega_1)$ and integrating over Ω_1 simplifies the left side of Eq. (A1) as well. Working out the terms we obtain

$$\sqrt{2}\int\langle\vec{r}_1|\langle\psi_{nl}|_2 \frac{\hat{p}_1^2}{2m}|\Psi_{12}\rangle Y_{00}(\Omega_1)\,d\Omega_1$$
$$= -\frac{\hbar^2}{2m}\frac{1}{r_1^2}\frac{d}{dr_1}\left(r_1^2\frac{dR_{1s}(r_1)}{dr_1}\right), \quad (A17)$$

$$\sqrt{2}\int\langle\vec{r}_1|\langle\psi_{nl}|_2 \frac{\hat{p}_2^2}{2m}|\Psi_{12}\rangle Y_{00}(\Omega_1)\,d\Omega_1$$
$$= \langle\psi_{nl}|\frac{\hat{p}^2}{2m}|\psi_{nl}\rangle R_{1s}(r_1) \equiv AR_{1s}(r_1), \quad (A18)$$

$$\sqrt{2}\int\langle\vec{r}_1|\langle\psi_{nl}|_2 \hat{V}_{N1}|\Psi_{12}\rangle Y_{00}(\Omega_1)\,d\Omega_1 = -\frac{2e^2}{r_1}R_{1s}(r_1), \quad (A19)$$

$$\sqrt{2}\int\langle\vec{r}_1|\langle\psi_{nl}|_2 \hat{V}_{N2}|\Psi_{12}\rangle Y_{00}(\Omega_1)\,d\Omega_1$$
$$= -\langle\psi_{nl}|\frac{2e^2}{r}|\psi_{nl}\rangle R_{1s}(r_1) \equiv BR_{1s}(r_1), \quad (A20)$$

$$\sqrt{2}\int\langle\vec{r}_1|\langle\psi_{nl}|_2 \hat{V}_{12}|\Psi_{12}\rangle Y_{00}(\Omega_1)\,d\Omega_1$$
$$= \int e^2 Y_{1m}^*(\Omega_2)\frac{R_{nl}^*(r_2)R_{nl}(r_2)}{|\vec{r}_1-\vec{r}_2|}Y_{1m}(\Omega_2)Y_{00}(\Omega_1)$$
$$\times Y_{00}(\Omega_1)\,d\Omega_1\,d\Omega_2\,r_2^2\,dr_2\,R_{1s}(r_1)$$
$$\pm \int e^2 Y_{1m}^*(\Omega_2)\frac{R_{nl}^*(r_2)R_{1s}(r_2)}{|\vec{r}_1-\vec{r}_2|}Y_{00}(\Omega_2)Y_{1m}(\Omega_1)$$
$$\times Y_{00}(\Omega_1)\,d\Omega_1\,d\Omega_2\,r_2^2\,dr_2\,R_{nl}(r_1). \quad (A21)$$

We make use of the identity

$$\frac{1}{|\vec{r}_1-\vec{r}_2|} = \sum_{lm}\frac{4\pi}{2l+1}Y_{lm}^*(\Omega_1)Y_{lm}(\Omega_2)\frac{r_<^l}{r_>^{l+1}} \quad (A22)$$

to handle the two integrals in the last expression. After integrating over all angles, each integral becomes a "potential function" (see Appendix B). One potential function is due to electrostatic screening, which we label in this case as $V_{Cnl}(r_1)$. The other function is referred to as an exchange interaction, which we label as $V_x(r_1)$. Putting all the terms together, we have a differential equation that contains $R_{1s}(r)$ and $R_{nl}(r)$

$$-\frac{\hbar^2}{2m}\frac{1}{r_1^2}\frac{d}{dr_1}\left(r_1^2\frac{dR_{1s}(r_1)}{dr_1}\right) - \frac{2e^2}{r_1}R_{1s}(r_1)$$
$$+ V_{Cnl}(r_1)R_{1s}(r_1)\pm V_x R_{nl}(r_1) = (E-A-B)R_{1s}(r_1). \quad (A23)$$

As with the ground state, for brevity we replace r_1 with r and define $u(r) = rR(r)$. With these substitutions, we end up with the differential equation that we will solve numerically

$$-\frac{\hbar^2}{2m}\frac{d^2 u_{1s}(r)}{dr^2} - \frac{2e^2}{r}u_{1s}(r) + V_{Cnl}(r)u_{1s}(r)$$
$$\pm V_x(r)u_{nl}(r) = E'u_{1s}(r), \quad (A24)$$

where $E' \equiv E - A - B$. In terms of u_{nl}, A and B are

$$A = -\frac{\hbar^2}{2m}\int u_{nl}(r')\left(\frac{d^2 u_{nl}(r')}{dr'^2} - \frac{l(l+1)u_{nl}}{r'^2}\right)dr' \quad (A25)$$

and

$$B = -2e^2\int\frac{u_{nl}^2(r')}{r'}\,dr', \quad (A26)$$

since $u_{nl}(r)$ is real.

In Eq. (A24), there are two functions to be determined, $u_{1s}(r)$ and $u_{nl}(r)$, so we need another equation. A differential equation that contains derivatives of $u_{nl}(r)$ can be obtained in a similar manner as we did for $u_{1s}(r)$. First, we apply the bra $\sqrt{2}\langle\vec{r}_1|\langle\psi_{1s}|_2$ to each side of the Hamiltonian eigenvalue equation. Then we multiply each side of the equation by $Y_{lm}^*(\Omega_1)$ and integrate over Ω_1 to project out $R_{nl}(r_1)$. Similar to the $R_{1s}(r_1)$ case, the right side of Eq. (A1) becomes

$$\sqrt{2}\int\langle\vec{r}_1|\langle\psi_{1s}|_2 E|\Psi_{12}\rangle Y_{lm}^*(\Omega_1)\,d\Omega_1 = ER_{nl}(r_1). \quad (A27)$$

For the terms on the left side of Eq. (A1), we obtain the following results:

$$\sqrt{2}\int\langle\vec{r}_1|\langle\psi_{1s}|_2 \frac{\hat{p}_1^2}{2m}|\Psi_{12}\rangle Y_{lm}^*(\Omega_1)\,d\Omega_1$$
$$= -\frac{\hbar^2}{2m}\left[\frac{1}{r_1^2}\frac{d}{dr_1}\left(r_1^2\frac{dR_{nl}(r_1)}{dr_1}\right) - \frac{l(l+1)R_{nl}(r_1)}{r_1^2}\right], \quad (A28)$$

$$\sqrt{2}\int \langle \vec{r}_1 | \langle \psi_{1s}|_2 \frac{\hat{p}_2^2}{2m}|\Psi_{12}\rangle Y_{lm}^*(\Omega_1)\, d\Omega_1$$

$$= \langle \psi_{1s}| \frac{\hat{p}^2}{2m}|\psi_{1s}\rangle R_{nl}(r_1) \equiv A' R_{nl}(r_1), \qquad (A29)$$

$$\sqrt{2}\int \langle \vec{r}_1 | \langle \psi_{1s}|_2 \hat{V}_{N1}|\Psi_{12}\rangle Y_{lm}^*(\Omega_1)\, d\Omega_1 = -\frac{2e^2}{r_1}R_{nl}(r_1), \qquad (A30)$$

$$\sqrt{2}\int \langle \vec{r}_1 | \langle \psi_{1s}|_2 \hat{V}_{N2}|\Psi_{12}\rangle Y_{lm}^*(\Omega_1)\, d\Omega_1$$

$$= -\langle \psi_{1s}|\frac{2e^2}{r}|\psi_{1s}\rangle R_{nl}(r_1) \equiv B' R_{nl}(r_1), \qquad (A31)$$

$$\sqrt{2}\int \langle \vec{r}_1 | \langle \psi_{1s}|_2 \hat{V}_{12}|\Psi_{12}\rangle Y_{lm}^*(\Omega_1)\, d\Omega_1$$

$$= \int e^2 Y_{00}^*(\Omega_2)\frac{R_{1s}^*(r_2)R_{1s}(r_2)}{|\vec{r}_1 - \vec{r}_2|}Y_{00}(\Omega_2)Y_{lm}(\Omega_1)$$

$$\times Y_{lm}^*(\Omega_1)\, d\Omega_1\, d\Omega_2\, r_2^2\, dr_2\, R_{nl}(r_1)$$

$$\pm \int e^2 Y_{00}^*(\Omega_2)\frac{R_{1s}^*(r_2)R_{nl}(r_2)}{|\vec{r}_1 - \vec{r}_2|}Y_{lm}(\Omega_2)Y_{00}(\Omega_1)$$

$$\times Y_{lm}^*(\Omega_1)\, d\Omega_1\, d\Omega_2\, r_2^2\, dr_2\, R_{1s}(r_1). \qquad (A32)$$

The two integrals in the last expression can be simplified, as shown in Appendix B. After integrating over angles, one is left with two potential functions as before. One potential function is due to electrostatic screening from the $1s$ electron, which we label in this case as $V_{C1s}(r_1)$. The other function is an exchange interaction, which we label as $V_x(r_1)$, and is the same as in the equation for u_{1s}. Putting all the terms together, we have a second differential equation that contains $R_{nl}(r)$ and $R_{1s}(r)$

$$-\frac{\hbar^2}{2m}\left[\frac{1}{r_1^2}\frac{d}{dr_1}\left(r_1^2\frac{dR_{nl}(r_1)}{dr_1}\right) - \frac{l(l+1)}{r_1^2}R_{nl}(r_1)\right]$$

$$-\frac{2e^2}{r_1}R_{nl}(r_1) + V_{C1s}(r_1)R_{nl}(r_1) \pm V_x R_{1s}(r_1)$$

$$= (E - A' - B')R_{nl}(r_1). \qquad (A33)$$

As with the ground state, we can replace r_1 with r and define $u(r) = rR(r)$. With these substitutions, we end up with the differential equation that we will solve numerically

$$-\frac{\hbar^2}{2m}\left(\frac{d^2u_{nl}(r)}{dr^2} - \frac{l(l+1)}{r^2}u_{nl}(r)\right) - \frac{2e^2}{r}u_{nl}(r)$$

$$+ V_{C1s}(r)u_{nl}(r) \pm V_x(r)u_{1s}(r) = E''u_{nl}(r), \qquad (A34)$$

where $E'' \equiv E - A' - B'$. In terms of u_{1s}, A' and B' are

$$A' = -\frac{\hbar^2}{2m}\int u_{1s}(r')\frac{d^2u_{1s}(r')}{dr'^2}\, dr' \qquad (A35)$$

and

$$B' = -2e^2 \int \frac{u_{1s}^2(r')}{r'}\, dr', \qquad (A36)$$

since $u_{1s}(r)$ is real.

We note that for the excited $1snl$ states, there are two ways to obtain the energy E: $E = E'' + A' + B'$ and $E = E' + A + B$. By comparing the two values for E, $E'' + A' + B'$ with $E' + A + B$, we can check on the numerical accuracy of the calculation.

APPENDIX B: SCREENING AND EXCHANGE POTENTIALS

The screening and exchange potentials are critical ingredients in the coupled Schrödinger equations for the atomic states of helium. We are interested in helium atomic states that have $l = 0$ for at least one electron. For these atomic states, the screening and exchange potentials each contain only one term, simplifying the calculations. We obtain the potentials by using the identity

$$\frac{1}{|\vec{r}_1 - \vec{r}_2|} = \sum_{LM}\frac{4\pi}{2L+1}\frac{r_<^L}{r_>^{L+1}}Y_{LM}^*(\Omega_1)Y_{LM}(\Omega_2), \qquad (B1)$$

where $r_<$ is the smaller of r_1 and r_2, and $r_>$ is the larger of r_1 and r_2.

Consider first the screening potential V_{Cnl}, when the nl electron screens out the $1s$ electron in Eq. (A24). From Appendix A, V_{Cnl} is proportional to the following integral:

$$V_{Cnl}(r_1) \propto \int R_{nl}(r_2)Y_{lm}^*(\Omega_2)\frac{1}{|\vec{r}_1 - \vec{r}_2|}R_{nl}(r_2)$$

$$\times Y_{lm}(\Omega_2)Y_{00}(\Omega_1)Y_{00}^*(\Omega_1)r_2^2\, d\Omega_1\, d\Omega_2\, dr_2. \qquad (B2)$$

After integrating over Ω_1, only the $L = 0$ term in the expression for $1/|\vec{r}_1 - \vec{r}_2|$ survives, leaving the following integral over the $\vec{r}_2$ coordinate:

$$V_{Cnl}(r_1) \propto \int R_{nl}(r_2)Y_{lm}^*(\Omega_2)\frac{1}{r_>}Y_{00}(\Omega_2)R_{nl}(r_2)$$

$$\times Y_{lm}(\Omega_2)r_2^2\, d\Omega_2\, dr_2. \qquad (B3)$$

After integrating over the angle Ω_2, we are left with the integral over r_2

$$V_{Cnl}(r_1) \propto \int R_{nl}^2(r_2)\frac{1}{r_>}r_2^2\, dr_2, \qquad (B4)$$

since Y_{00} is a constant and $R_{nl}(r_2)$ is real. We can replace r_1 with r and r_2 with r' to give

$$V_{Cnl}(r) \propto \int R_{nl}^2(r')\frac{1}{r_>}r'^2\, dr'. \qquad (B5)$$

If $r > r'$ then $r_> = r$, and if $r' > r$ then $r_> = r'$. We note that this integral is proportional to the electrostatic potential due to a spherically symmetric charge distribution of density $R_{nl}^2(r')$.

Now consider the other screening potential. When the $1s$ electron screens out the nl electron in Eq. (A34), the screening potential for the radial component is determined from the following integral:

$$V_{C1s}(r_1) \propto \int R_{1s}^*(r_2) Y_{00}^*(\Omega_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} R_{1s}(r_2)$$
$$\times Y_{00}(\Omega_2) Y_{lm}(\Omega_1) Y_{lm}^*(\Omega_1) r_2^2 \, d\Omega_1 \, d\Omega_2 \, dr_2. \tag{B6}$$

In this case, one integrates first over Ω_2 and only the $L = 0$ term in the expression for $1/|\vec{r}_1 - \vec{r}_2|$ survives, leaving the following integral:

$$V_{C1s}(r_1) \propto \int R_{1s}^*(r_2) \frac{1}{r_>} R_{1s}(r_2) Y_{lm}(\Omega_1) Y_{lm}^*(\Omega_1) r_2^2 \, d\Omega_1 \, dr_2. \tag{B7}$$

Integrating over Ω_1 and using the orthogonality property of the spherical harmonics gives

$$V_{C1s}(r_1) \propto \int R_{1s}^*(r_2) \frac{1}{r_>} R_{1s}(r_2) r_2^2 \, dr_2. \tag{B8}$$

We can replace r_1 with r and r_2 with r' to give

$$V_{C1s}(r) \propto \int R_{1s}^2(r') \frac{1}{r_>} r'^2 \, dr'. \tag{B9}$$

As before, $V_{C1s}(r)$ is the electrostatic potential from a spherical charge distribution with density proportional to R_{1s}^2.

Since the Coulomb screening potentials $V_{C1s}(r)$ and $V_{Cnl}(r)$ are electrostatic potentials from spherically symmetric charge distributions, they are relatively easy to determine numerically. One doesn't need to work out the integral, but can instead use Gauss's law, which gives $\vec{E}(r) = E(r)\hat{r} \propto (Q_{<r}/r^2)\hat{r}$ for a spherically symmetric charge distribution, where $Q_{<r}$ is the charge contained inside a sphere of radius r. Since $E(r) = -dV/dr$, the potential satisfies the differential equation

$$\frac{dV}{dr} \propto -\frac{Q_{<r}}{r^2}, \tag{B10}$$

with the boundary condition that for values of r outside the atom $V(r) = e^2/r$. Numerically, $V(i)$ can be computed by first setting the charge Q and $V(0)$ equal to zero. If i is increased in a loop from 1 out to $i_{\max}$, the following two lines of code, $Q \leftarrow Q + u(i)^2 \Delta$ and $V(i) \leftarrow V(i-1) - eQ[\Delta/r(i)]/r(i)$, will update the charge less than r and the Coulomb potential $V(i)$. Adding the constant $e^2/r(i_{\max}) - V(i_{\max})$ to all $V(i)$ will give the correct boundary condition $V(r \to \infty) \to e^2/r$.[18]

Now consider the exchange potential for an nl excited state. The potential is proportional to the integral

$$V_x(r_1) \propto \int R_{1s}^*(r_2) Y_{00}^*(\Omega_2) \frac{1}{|\vec{r}_1 - \vec{r}_2|} R_{nl}(r_2)$$
$$\times Y_{lm}(\Omega_2) Y_{00}(\Omega_1) Y_{lm}^*(\Omega_1) r_2^2 \, d\Omega_1 \, d\Omega_2 \, dr_2. \tag{B11}$$

After integrating over Ω_1, only the $L = l$ term in the expression for $1/|\vec{r}_1 - \vec{r}_2|$ survives, leaving the following integral over the $\vec{r}_2$ coordinate:

$$V_x(r_1) \propto \int R_{1s}^*(r_2) Y_{00}^*(\Omega_2) \frac{r_<^l}{r_>^{l+1}} Y_{lm}^*(\Omega_2)$$
$$\times R_{nl}(r_2) Y_{lm}(\Omega_2) r_2^2 \, d\Omega_2 \, dr_2. \tag{B12}$$

Integrating over Ω_2 yields

$$V_x(r_1) \propto \int R_{1s}^*(r_2) \frac{r_<^l}{r_>^{l+1}} R_{nl}(r_2) r_2^2 \, dr_2, \tag{B13}$$

since Y_{00} is a constant. Replacing r_1 with r and r_2 with r', we have

$$V_x(r) \propto \int R_{1s}(r') R_{nl}(r') \frac{r_<^l}{r_>^{l+1}} r'^2 \, dr', \tag{B14}$$

since the radial functions are real. Note that the exchange potential is the same for u_{1s} and u_{nl}.

Determining the exchange potential by carrying out this integral can be computationally intensive because for every value of r, one needs to integrate r' out to infinity. For the Coulomb screening potentials, V_{C1s} and V_{Cnl}, one can use Gauss's law. However, for the exchange potential there is another factor of l in the integral, and one would need to solve the integral for $V_x(r)$.

We use another method for obtaining V_x, which requires solving a differential equation rather than an integral. The potential V_x is a solution to Poisson's equation for angular momentum l and charge density proportional to $R_{1s}(r)R_{nl}(r)$

$$\frac{1}{r^2} \frac{d}{dr}\left(r^2 \frac{dV_x(r)}{dr} \right) - \frac{l(l+1)}{r^2} V_x(r) = R_{1s}(r) R_{nl}(r). \tag{B15}$$

If we let $R_i(r) = u_i(r)/r$ and $V_x(r) = w_x(r)/r$, the equation simplifies to

$$\frac{d^2 w_x(r)}{dr^2} - \frac{l(l+1)}{r^2} w_x(r) = \frac{u_{1s}(r) u_{nl}(r)}{r}. \tag{B16}$$

The boundary conditions on w_x are $w_x(0) = 0$ and $w_x(r \to \infty) \to Q_l/r^l$, where

$$Q_l = \int \frac{u_{1s}(r') u_{nl}(r')}{2l+1} r'^l \, dr', \tag{B17}$$

which determines the proportionality constant.

In our code, we iterate out two solutions $w_A(r)$ and $w_B(r)$, where $w_A(0) = w_B(0) = 0$ and $w_A(1)$ is different than $w_B(1)$. The potential w_x is a linear combination of w_A and w_B: $w_x(r) = a w_A(r) + b w_B(r)$. The constants a and b are determined by the boundary conditions at large r. To do this, we pick two values of r: r_1 and r_2, which are far outside the charge distribution. The two equations for these r values,

$$\frac{Q_l}{r_1^l} = a w_A(r_1) + b w_B(r_1), \tag{B18}$$

$$\frac{Q_l}{r_2^l} = a w_A(r_2) + b w_B(r_2), \tag{B19}$$

can be solved for the constants a and b

$$a = Q_l \frac{r_2^l w_B(r_2) - r_1^l w_B(r_1)}{r_1^l r_2^l (w_A(r_1) w_B(r_2) - w_A(r_2) w_B(r_1))}, \tag{B20}$$

$$b = Q_l \frac{r_1^l w_A(r_1) - r_2^l w_A(r_2)}{r_1^l r_2^l (w_A(r_1) w_B(r_2) - w_A(r_2) w_B(r_1))}. \tag{B21}$$

The potential is given by

$$V_x(r) = \frac{a w_A(r) + b w_B(r)}{r}. \tag{B22}$$

As a check one can calculate the two screening potentials in the same manner as the exchange potential $V_x(r)$. The only difference in the calculation is that the "exchange density" $R_{1s}(r) R_{nl}(r)$ is replaced by the "screening density" $R_{1s}^2(r)$ or $R_{nl}^2(r)$. Whereas the Coulomb screening potentials are fairly easy to obtain using Gauss's law, the exchange potential is not. However, the use of Poisson's equation makes the helium problem tractable as an undergraduate physics student exercise.

APPENDIX C: ORTHOGONALITY OF 1sns TRIPLET RADIAL FUNCTIONS

We have been considering the following ansatz for the excited states of helium:

$$|\Psi_{12}\rangle = \frac{1}{\sqrt{2}} \left(|\psi_{1s}\rangle_1 |\psi_{nl}\rangle_2 \pm |\psi_{nl}\rangle_1 |\psi_{1s}\rangle_2 \right). \tag{C1}$$

The simple separation into two coupled differential equations carried out in Appendix A required $\langle \psi_{1s} | \psi_{nl} \rangle$ to equal zero. If this is the case, then the only term that couples the two differential equations is the exchange potential, and the excited-state energies can be obtained as described in the text. If $l \neq 0$, that is, for the excited p and d states, the integral over angle Ω yields zero due to the orthogonality of the spherical harmonics. However, for excited s states the angular integral is not zero and the radial functions must be orthogonal to make $\langle 1s | ns \rangle = 0$. Here, we show that for the 1sns triplet excited states, the coupled differential equations are consistent with $\langle 1s | ns \rangle = 0$.

The inner product $\langle 1s | ns \rangle$ is proportional to $\int R_{1s}(r) R_{ns}(r) r^2 \, dr$, or in terms of the functions $u(r) = rR(r)$, $\langle 1s | ns \rangle$ is proportional to $\int u_{1s}(r) u_{ns}(r) \, dr$. Suppose $u_{1s}(r)$ and $u_{ns}(r)$ are solutions to the desired coupled Schrödinger equations,

$$\frac{d^2 u_{1s}(r)}{dr^2} - \frac{2e^2}{r} u_{1s}(r) + e^2 \int \frac{u_{ns}(r') u_{ns}(r')}{|\vec{r} - \vec{r'}|} \, d\Omega' \, dr' \, u_{1s}(r)$$
$$\pm e^2 \int \frac{u_{1s}(r') u_{ns}(r')}{|\vec{r} - \vec{r'}|} \, d\Omega' \, dr' \, u_{ns}(r) = E_1 u_{1s}(r) \tag{C2}$$

and

$$\frac{d^2 u_{ns}(r)}{dr^2} - \frac{2e^2}{r} u_{ns}(r) + e^2 \int \frac{u_{1s}(r') u_{1s}(r')}{|\vec{r} - \vec{r'}|} \, d\Omega' \, dr' \, u_{ns}(r)$$
$$\pm e^2 \int \frac{u_{1s}(r') u_{ns}(r')}{|\vec{r} - \vec{r'}|} \, d\Omega' \, dr' \, u_{1s}(r) = E_2 u_{ns}(r), \tag{C3}$$

as derived in Appendix A. The energies are $E_1 = E - A - B$ and $E_2 = E - A' - B'$, where A, B, A', and B' are defined in Appendix A. Note that in general $E_1 \neq E_2$.

We show next that the triplet state ($-$sign) solution is consistent with $\int u_{1s}(r) u_{ns}(r) \, dr = 0$. Start by multiplying Eq. (C2) by $u_{ns}(r)$ and integrate over r

$$\int u_{ns}(r) \frac{d^2 u_{1s}(r)}{dr^2} \, dr - \int u_{ns}(r) \frac{2e^2}{r} u_{1s}(r) \, dr$$
$$+ e^2 \int \int \frac{u_{ns}(r') u_{ns}(r')}{|\vec{r} - \vec{r'}|} \, d\Omega' \, dr' \, u_{1s}(r) u_{ns}(r) \, dr$$
$$\pm e^2 \int \int \frac{u_{1s}(r') u_{ns}(r')}{|\vec{r} - \vec{r'}|} \, d\Omega' \, dr' \, u_{ns}(r) u_{ns}(r) \, dr$$
$$= E_1 \int u_{1s}(r) u_{ns}(r) \, dr. \tag{C4}$$

Note that the double integrals are actually equal to each other. Since both u_{1s} and u_{ns} do not depend on angle, only the $l = 0$ term in $1/|\vec{r} = \vec{r'}|$ survives the integration over Ω'. Also $|\vec{r} - \vec{r'}| = |\vec{r'} - \vec{r}|$, and after integrating over Ω', the screening double integral equals

$$\int \int \frac{u_{ns}(r') u_{ns}(r') u_{ns}(r) u_{1s}(r)}{r_>} \, dr \, dr' \tag{C5}$$

and the exchange double integral equals

$$\int \int \frac{u_{1s}(r') u_{ns}(r') u_{ns}(r) u_{ns}(r)}{r_>} \, dr \, dr', \tag{C6}$$

and these are equal to each other because we can interchange r and r' in either integral. Thus, for the triplet case the double integrals cancel and Eq. (C4) reduces to

$$\int u_{ns}(r) \frac{d^2 u_{1s}(r)}{dr^2} \, dr - \int u_{ns}(r) \frac{2e^2}{r} u_{1s}(r) \, dr$$
$$= E_1 \int u_{1s}(r) u_{ns}(r) \, dr. \tag{C7}$$

If we multiply Eq. (C3) by u_{1s} and integrate over r as we did with Eq. (C2), the double integrals will also cancel for the triplet case. Equation (C3) reduces to

$$\int u_{1s}(r) \frac{d^2 u_{ns}(r)}{dr^2} \, dr - \int u_{1s}(r) \frac{2e^2}{r} u_{ns}(r) \, dr$$
$$= E_2 \int u_{ns}(r) u_{1s}(r) \, dr. \tag{C8}$$

If we subtract Eqs. (C7) and (C8), the kinetic energy terms cancel

$$\int u_{ns}(r) \frac{d^2 u_{1s}(r)}{dr^2} \, dr = - \int \frac{du_{ns}}{dr} \frac{du_{1s}}{dr} \, dr$$
$$= \int u_{1s}(r) \frac{d^2 u_{ns}(r)}{dr^2} \, dr, \tag{C9}$$

where we have integrated by parts twice and used $u_{1s}(\infty) = u_{ns}(\infty) = 0$. Also, the Coulomb potential terms cancel in the subtraction

$$\int \frac{2e^2 u_{ns}(r) u_{1s}(r)}{r} \, dr - \int \frac{2e^2 u_{1s}(r) u_{ns}(r)}{r} \, dr = 0. \tag{C10}$$

Thus, after integrating and subtracting the two equations one is left with

$$(E_1 - E_2) \int u_{1s}(r) u_{ns}(r) \, dr = 0. \tag{C11}$$

Since $E_1 \neq E_2$, the two radial triplet wave functions must be orthogonal.

In the case of the singlet, the + sign between the screening and exchange term results in an addition of these two equal double integral terms in Eq. (C4). However, the double integral resulting from Eq. (C2) contains the product $u_2(r')u_2(r')u_2(r)u_1(r)$, whereas the double integral term resulting from Eq. (C3) has the product $u_1(r')u_1(r')u_1(r)u_2(r)$. These two products are not in general equal and do not cancel in the subtraction of the two equations. After subtracting the equations, we are left with

$$
\begin{aligned}
(E_1 - E_2) &\int u_{1s}(r) u_{ns}(r) \, dr \\
&= 2 \int \int \frac{u_{1s}(r') u_{ns}(r') u_{ns}(r) u_{ns}(r)}{r_>} \, dr \, dr' \\
&\quad - 2 \int \int \frac{u_{ns}(r') u_{1s}(r') u_{1s}(r) u_{1s}(r)}{r_>} \, dr \, dr',
\end{aligned} \tag{C12}
$$

and $\int u_{1s}(r) u_{ns}(r) \, dr \neq 0$ in general for the solutions to Eqs. (C2) and (C3) with the + sign (i.e., singlet excited s states). In this case, the coupled differential equations will have many cross terms, making the calculation too difficult for an undergraduate exercise.

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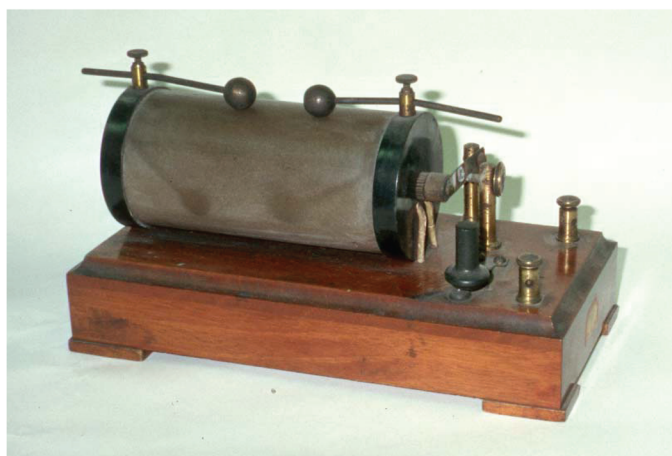
Induction Coil

This little induction coil, only 23 cm in length, is unmarked, but is typical of instruments sold to the secondary school market in the first quarter of the 20th century. For about $20, you could get a coil that would drive a Maltese cross tube, a railway tube or a tube to demonstrate the heating effects of cathode rays, thus showing students the properties of cathode rays (electrons). Of course, these demonstrations also produced x rays… This instrument is in the Greenslade Collection. (Notes and picture by Thomas B. Greenslade, Jr., Kenyon College)