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Estimating the energies and splitting of the $1s2s$ singlet and triplet states of helium is a classic exercise in quantum perturbation theory but yields only qualitatively correct results. Using a six-line computer program, the $1s2s$ energies calculated by matrix diagonalization using a seven-state basis improve the results to 0.4% error or better. This is an effective and practical illustration of the quantitative power of quantum mechanics, at a level accessible to undergraduate students. © *2015 American Association of Physics Teachers.*
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I. INTRODUCTION

The energy level structure of helium is a classic problem in quantum mechanics and was historically important in confirming of the correctness of quantum theory.[1] It serves as an excellent textbook example of the variational method, first-order perturbation theory, and exchange symmetry.[2,3] However, the accuracy attained in textbook calculations is modest to poor; for example, the first-order perturbative estimate of the $1s2s$ singlet-triplet splitting is too large by a factor of 3. Students are often left with the impression that accurate results require advanced methods.

With the power and ease of use of modern scientific computing software such as MATHEMATICA (Ref. 4) or MATLAB (Ref. 5), however, it is well within the ability of an upper-level undergraduate to make sub-percent-accuracy calculations of the low-lying energies by straightforward matrix diagonalization. We illustrate here by calculating the energies of the $1s2s$ singlet and triplet states.

The standard perturbation theory approach writes the He atom Hamiltonian as $H = H^0 + V$, with

$$H^0 = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{2}{r_1} - \frac{2}{r_2} \tag{1}$$

and

$$V = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{1}{r_{12}}, \tag{2}$$

where $\mathbf{r}_i$ is the position vector for electron i. Atomic (hartree) units are used here and throughout.[6] We note that H^0 is the Hamiltonian for two non-interacting electrons moving outside an alpha particle nucleus, with the position-space representation of the eigenstates given by

$$
\begin{aligned}
&\langle \mathbf{r}_1 \mathbf{r}_2 | n_1 l_1 n_2 l_2 \rangle \\
&= \frac{P_{n_1 l_1}(r_1)}{r_1}\frac{P_{n_2 l_2}(r_2)}{r_2}Y_{l_1 m_1}(\theta_1,\phi_1)Y_{l_2 m_2}(\theta_2,\phi_2),
\end{aligned} \tag{3}
$$

where $Y_{lm}(\theta,\phi)$ is the standard spherical harmonic, $P_{nl}(r)$ is the He$^+$ (reduced) radial wavefunction

$$P_{nl}(r) = \sqrt{\frac{2(n-l-1)!}{n^2(n+l)!}}\left(\frac{4r}{n}\right)^{l+1}e^{-2r/n}L_{n-l-1}^{2l+1}(4r/n), \tag{4}$$

and $L_p^a(r)$ are generalized pth-order Laguerre polynomials.[7] The corresponding unperturbed energies, which depend only on the principal quantum numbers, are

$$E_{n_1,n_2}^0 = -\frac{2}{n_1^2} - \frac{2}{n_2^2}. \tag{5}$$

The usual textbook calculation[3] shows that, to first order in the perturbation, the energies of the $1s2s\,{}^1S_0$ and $1s2s\,{}^3S_1$ states can be written in terms of direct ($J = \langle 1s2s|V|1s2s\rangle$) and exchange ($K = \langle 1s2s|V|2s1s\rangle$) contributions

$$E_{1s2s} \approx E_{1,2}^0 + J \pm K = -2.08 \pm 0.04 \text{ a.u.}, \tag{6}$$

where $+$ gives the singlet (${}^1S_0$) energy and $-$ gives the triplet (${}^3S_1$) energy. The experimental energies[8] are -2.1604 ± 0.0146 a.u., or -58.788 ± 0.398 eV. So the error in $E_{1,2}^0 + J$ is 3.7%, while the calculated singlet-triplet splitting $2K$ is a factor of 3 larger than the experimental number.

In the following section, we describe the theoretical extensions required to produce a simple computer program that improves on perturbation theory by an order of magnitude or more. In particular, the error in the $1s2s$ singlet-triplet splitting is improved to 17%. It is likely that the remaining error is dominated by neglect of continuum states.

II. IMPROVED HELIUM ENERGIES

The problem with applying perturbation theory to the He atom is that the Coulomb repulsion between the electrons is not small; the off-diagonal matrix elements of V are often comparable in size to the unperturbed energy differences. Under these conditions, it is not a surprise that perturbation theory should not work well. Our approach is to diagonalize H in a basis of the eigenstates of H^0. Even so, it is not necessary to diagonalize a large matrix, because to a reasonably good approximation the He wave functions turn out to be combinations of only three or four basis states.

The simplest way to do the calculation is to use the unsymmetrized basis states $1s1s$, $1s2s$, $2s1s\ldots4s1s\ldots$. The matrix H^0 is diagonal, with elements E_{n_1,n_2}^0. The matrix elements $\langle n_1s\,n_2s|V|n_3s\,n_4s\rangle$ of V involve integrals over the radial and angular variables of both electrons. For s states, the angular integrals can be done by direct integration as shown by Townsend.[3] A more general approach exploits the expansion of $1/r_{12}$ in spherical harmonics,[9]

$$\frac{1}{r_{12}} = \sum_{lm} \frac{4\pi}{2l+1} \frac{r_<^l}{r_>^{l+1}} (-1)^m Y_{l,-m}(\Omega_1) Y_{lm}(\Omega_2) \quad (7)$$

$$= \frac{1}{r_>} + (l > 0 \text{ terms}), \quad (8)$$

where $r_>$ and $r_<$ are $\max(r_1, r_2)$ and $\min(r_1, r_2)$, respectively. This is equivalent to the binomial expansion expressed as a series of Legendre polynomials[10] and is very useful for problems in electro- and magneto-statics with spherical symmetry.[10,11] For our present calculation, only the $l = 0$ term is important so that the angular integrals are 1 and the matrix elements of V become

$$\langle n_1 s\, n_2 s | V | n_3 s\, n_4 s \rangle$$
$$= \int d^3 r_1 d^3 r_2\, P_{n_1 s}(r_1) P_{n_2 s}(r_2) \frac{1}{r_>} P_{n_3 s}(r_1) P_{n_4 s}(r_2). \quad (9)$$

These integrals can be done analytically or numerically using MATHEMATICA without any additional manipulation.

Using the truncated set of basis states $\{1s1s, 1s2s, 2s1s, 1s3s, 3s1s, 1s4s, 4s1s\}$ gives the Hamiltonian matrix (shown to three decimal places):

$$H = \begin{pmatrix}
-2.750 & 0.179 & 0.179 & 0.088 & 0.088 & 0.055 & 0.055 \\
0.179 & -2.080 & 0.044 & 0.101 & 0.022 & 0.057 & 0.014 \\
0.179 & 0.044 & -2.080 & 0.022 & 0.101 & 0.014 & 0.057 \\
0.088 & 0.101 & 0.022 & -2.023 & 0.012 & 0.058 & 0.007 \\
0.088 & 0.022 & 0.101 & 0.012 & -2.023 & 0.007 & 0.058 \\
0.055 & 0.057 & 0.014 & 0.058 & 0.007 & -2.010 & 0.005 \\
0.055 & 0.014 & 0.057 & 0.007 & 0.058 & 0.005 & -2.010
\end{pmatrix}. \quad (10)$$

The lowest three eigenvalues correspond to the ground state and the $1s2s$ triplet and singlet states. The lowest triplet state, with eigenvalue -2.17097, is within 0.2% of the experimental $1s2s\,^3S_1$ energy (-2.17503). The ground state energy (-2.84138) is 2% above the experimental value of -2.90339, while the $1s2s$ singlet energy (-2.13662) is 0.4% higher than experiment (-2.14577). The $1s2s\,^1S_0 - 1s2s\,^3S_1$ splitting is improved to 17% error, far superior to the factor of 3 error of perturbation theory. The remaining 2% error in the ground state is well known to result from neglect of higher-l and continuum states,[1] and we presume this is also the case for the errors in the $1s2s$ states.

The poor performance of perturbation theory for the excited states can be understood by inspection of the Hamiltonian and the $1s2s$ eigenvectors. The matrix element $\langle 1s2s | V | 1s3s \rangle = 0.1011$, while the difference $\langle 1s3s | H | 1s3s \rangle - \langle 1s2s | H | 1s2s \rangle = 0.0569$. This signals strong mixing between these states. The triplet eigenvector is

$$|1s2s\,^3S\rangle = (-1.302 \times 10^{-7}, 0.6198, -0.6198,$$
$$-0.3344, 0.3344, -0.0634, 0.0634)^T, \quad (11)$$

so that the $\langle 1s3s | 1s2s\,^3S_1 \rangle$ amplitude is only a factor of 1.85 smaller than the $\langle 1s2s | 1s2s\,^3S_1 \rangle$ amplitude. The $|1s2s\rangle$ and $|1s3s\rangle$ states are strongly mixed by the electron-electron repulsion.

III. IMPLEMENTATION IN AN UNDERGRADUATE QUANTUM MECHANICS COURSE

The current generation of students enjoys a great advantage over it predecessors, in that high-level programming languages such as MATHEMATICA and MATLAB have so much built-in capability that quite complicated calculations can be done with a minimum of programming sophistication. For the He atom, all that is needed to do the calculation in MATHEMATICA is six lines of code, shown in Fig. 1 and available as an electronic supplement to this paper.[12] One command generates the radial wave functions from built-in standard functions. Two lines implement the formulas for the matrix elements of H. The fourth line generates a list of the basis states used. The final two lines generate and diagonalize H.

In our course, the content of this paper was discussed in detail in class, and the program was provided to the students as a template. The students were then asked to calculate the energies of the $1s2p\,^1P_1$ and $1s2p\,^3P_J$ states. This introduces new features into the problem because the matrix element $\langle n_1 s\, n_2 p | V | n_3 s\, n_4 p \rangle$ comes from the $l = 0$ term of Eq. (7), while $\langle n_1 s\, n_2 p | V | n_3 p\, n_4 s \rangle$ comes from the $l = 1$ term. By constructing the Hamiltonian from $1snp$ basis states, the students discovered that while the $1s2p$ and $1s3p$ states are strongly mixed, contributions from higher-energy states are much smaller. This suggests that perturbation theory can be used to calculate the contributions from the higher $n_1 s n_2 p$ states and $n_1 p n_2 d$ states as well. Treatment of the latter case introduces yet another feature into the problem, namely, the need to use angular momentum addition rules to construct appropriate linear combinations of the various m_l states to produce an appropriate $L = 1$ state of the two electrons. This is excellent review of material covered earlier in the course, now applied to a specific and realistic problem. Most students, working in small groups for a few weeks, were able to reach better than 0.5% agreement with experiment.

There are many twists that one could imagine for projects based on the He atom. The students could be asked to use an

$$P_{n\_,1\_}[r\_] := \sqrt{\frac{(n-1-1)!\,2}{n^2\,((n+1)!)}}\;\left(\frac{4\,r}{n}\right)^{1+1} e^{-\frac{2\,r}{n}}\;\text{LaguerreL}\left[n-1-1,\,2\,1+1,\,\frac{4\,r}{n}\right]$$

$$V[\{n1\_,\,n2\_\},\,\{n3\_,\,n4\_\}] :=$$
$$\text{NIntegrate}\left[P_{n1,0}[r1]\,P_{n3,0}[r1]\,\text{Min}\left[\frac{1}{r2},\,\frac{1}{r1}\right]P_{n2,0}[r2]\,P_{n4,0}[r2],\,\{r2,\,0,\,\infty\},\,\{r1,\,0,\,\infty\}\right]$$

$$E0[\{n1\_,\,n2\_\}] := \frac{-2}{n1^2} + \frac{-2}{n2^2}$$

```
st = DeleteDuplicates[Table[{{1, i}, {i, 1}}, {i, 4}] ~ Flatten ~ 1]

H = DiagonalMatrix[E0 /@ st] + Table[V[st[[i]], st[[j]]], {i, Length[st]}, {j, Length[st]}]

eval = Eigenvalues[H][[ ;; 3]]
```

Fig. 1. MATHEMATICA code to calculate the low-lying S states of the He atom. An executable and annotated version is available electronically (Ref. 12).

explicitly symmetrized basis set, for example. Rather than using matrix diagonalization and perturbation theory, they could use the variational method for the ground state. Or the role of continuum states could be studied by using the He$^+$ basis states numerically calculated by enclosing the He$^+$ ion inside an imaginary box of $\sim$10 Å in diameter.[13,14] This approach gives a straightforward means of generating properly normalized continuum states and allows accuracy of the ground state energy to be improved to the 0.5% level. All of these variations have been successfully completed as student projects over the past few years.

IV. CONCLUSION

The He atom is an example of a realistic system than can be quantitatively understood using the methods learned in an introductory quantum mechanics course. Taking advantage of the power of computer software to make such calculations possible adds new dimensions to learning. Of course, in order to be effective the programming must be straightforward enough to not detract from concentrating on the physics. This problem nicely fits within these constraints.

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[1] Egil A. Hylleraas, "Reminiscences from early quantum mechanics of two-electron atoms," Rev. Mod. Phys. **35**, 421–430 (1963).

[2] Hallstein Høgaasen, Jean-Marc Richard, and Paul Sorba, "Two-electron atoms, ions, and molecules," Am. J. Phys. **78**(1), 86–93 (2010).

[3] John S. Townsend, *A Modern Approach to Quantum Mechanics* (University Science Books, Sausalito, CA, 2000), pp. 345–355.

[4] Wolfram Research, Inc., *Mathematica*, <http://www.wolfram.com/mathematica/>.

[5] The MathWorks, Inc., *MATLAB*, <http://www.mathworks.com/products/matlab/>.

[6] Boon K. Teo and Wai-Kee Li, "The scales of time, length, mass, energy, and other fundamental physical quantities in the atomic world and the use of atomic units in quantum mechanical calculations," J. Chem. Ed. **88**, 921–928 (2011). Reduced mass corrections, which are at the 0.01% level, are ignored.

[7] Warning: notations and normalizations for the Laguerre polynomials vary widely and should always be checked.

[8] A. Kramida, Yu. Ralchenko, J. Reader, and NIST ASD Team, "NIST Atomic Spectra Database (version 5.2)," <http://physics.nist.gov/PhysRefData/ASD/levels_form.html> (2014).

[9] Mitchel Weissbluth, *Atoms and Molecules* (Academic Press, New York, 1980), pp. 3–12.

[10] David J. Griffiths, *Introduction to Electrodynamics*, 3rd ed. (Pearson, New York, 1998), p. 153.

[11] John David Jackson, *Classical Electrodynamics*, 3rd ed. (Wiley, Hoboken, NJ, 1999), pp. 101–104.

[12] The Mathematica code that performs the calculations is available at http://dx.doi.org/10.1119/1.4921821 or at <http://digital.library.wisc.edu/1793/67881>.

[13] Mohandas Pillai, Joshua Goglio, and Thad G. Walker, "Matrix Numerov method for solving Schrödinger's equation," Am. J. Phys. **80**(11), 1017–1019 (2012).

[14] B. A. Jugdutt and F. Marsiglio, "Solving for three-dimensional central potentials using numerical matrix methods," Am. J. Phys. **81**(5), 343–350 (2013).