

Physics 221B
Spring 2011
Notes 28
Helium and Helium-like Atoms

1. Introduction

In these notes we treat helium and helium-like atoms, which are systems consisting of one nucleus and two electrons. If the nuclear charge is $Z = 2$, then we are dealing with ordinary helium, while $Z = 3$ is the Li^+ ion, $Z = 4$ is the Be^{++} ion, etc. In recent years there has been some interest in helium-like uranium, the ion U^{90+} , with $Z = 92$, for tests of quantum electrodynamics. A case not to be overlooked is $Z = 1$, a system consisting of a hydrogen nucleus plus two electrons. This system certainly has unbound states, for example, the states in electron-hydrogen scattering. It is not obvious that it possesses bound states, however, since it is not clear that one proton is capable of binding two electrons. In fact, a bound state of this system does exist, the H^- ion, which can be thought of as an electron bound to an otherwise neutral hydrogen atom. The second electron is rather weakly bound, as we shall see. The ion H^- plays an important role in applications, for example, in energy transport in stellar atmospheres. It is also used in proton accelerators to defeat Liouville's theorem in the process of filling up accelerating rings. In the following discussion of helium-like atoms we focus mostly on the bound states, but some attention is also given to the unbound states.

2. The Basic Hamiltonian

In these notes we work in atomic units, $e = m = \hbar = 1$. Placing the origin of a system of coordinates at the nucleus of charge Z and letting \mathbf{r}_1 and \mathbf{r}_2 be the positions of the two electrons, the basic Hamiltonian describing the helium-like system is

$$H = \frac{|\mathbf{p}_1|^2}{2} + \frac{|\mathbf{p}_2|^2}{2} - \frac{Z}{r_1} - \frac{Z}{r_2} + \frac{1}{r_{12}}. \quad (1)$$

Here $r_1 = |\mathbf{r}_1|$, $r_2 = |\mathbf{r}_2|$, and $r_{12} = |\mathbf{r}_2 - \mathbf{r}_1|$.

This Hamiltonian incorporates all the nonrelativistic, electrostatic effects in helium, but it omits a number of small effects and makes some approximations. The approximation in the use of the Hamiltonian (1) is numerically quite good, but there is some interesting physics in the neglected terms and consideration of them leads to an improved understanding of some of the steps we take in solving the approximate system.

First, the frame attached to the nucleus is not really an inertial frame, since the nucleus is pulled by the electric forces from the electrons and accelerates somewhat in response. However, since the mass of the nucleus is large in comparison to the mass of the electron, the corrections, which are

known as “mass polarization” terms, are small. Similar corrections result from ignoring the small difference between the true electron mass and the reduced mass of the electron and the nucleus. Both these corrections are of order of the electron to nucleus mass ratio, which is approximately 10^{-4} in helium.

Second, there are a variety of fine structure terms which, as in hydrogen, can be thought of as relativistic corrections. These are all of order α^2 or $(Z\alpha)^2$, and are roughly of order 10^{-3} to 10^{-4} in helium. (But as in hydrogen, fine structure effects grow with Z , and are much more important in heavier atoms.) In addition to the relativistic kinetic energy correction, the Darwin term and the spin-orbit term, all of which are present in hydrogen, there are also terms representing the interaction of one electron with the magnetic field produced by the orbital motion of the other electron (spin-other-orbit terms), or produced by the magnetic moment of the other electron (spin-spin terms). There are also terms taking into account retardation in the communication between the two electrons.

Third, there are interactions with the quantized electromagnetic field, generalizations of the Lamb shift in hydrogen.

Finally, there may be hyperfine interactions between the electron and the multipole moments of the nucleus (but not in ordinary helium, since the α -particle has spin 0).

With the neglect of all these small terms, the basic helium-like Hamiltonian (1) is a purely spatial operator, and does not involve the spin. Thus, it is similar in its level of approximation to the electrostatic model of hydrogen. Due to the requirements of the symmetrization postulate, however, spin plays a significant role in the structure of helium, much more so than in hydrogen at a similar level of approximation.

3. Wave Functions and Hilbert Spaces

In this section we review the meaning of the tensor product of Hilbert spaces, we show how it works out in the case of helium and how to think of wave functions for helium, and we clarify some common terminology, such as “the spin (or spatial) part of the wave function,” which can be confusing. This terminology has definite limitations, which it is important to be aware of. We also explain why the eigenfunctions of the Hamiltonian (1) are products of spatial times spin wave functions with opposite symmetry under exchange, and what the limitations are of that statement.

The helium Hamiltonian (1) acts on a space of kets or wave functions (that is, a Hilbert space) for two identical electrons. To understand this two-electron Hilbert space, we start with the Hilbert space for a single electron. This is the product of an orbital (or spatial) Hilbert space times a spin Hilbert space for a single particle:

$$\mathcal{E} = \mathcal{E}_{\text{orb}} \otimes \mathcal{E}_{\text{spin}} \quad (\text{single particle}). \quad (2)$$

This space is spanned by the basis kets $|\mathbf{r}\rangle \otimes |m\rangle = |\mathbf{r}m\rangle$, where \mathbf{r} runs over three-dimensional space and $m = \pm\frac{1}{2}$.

The two-electron Hilbert space \mathcal{E}_{tot} is the product of two identical copies of the single-electron Hilbert space,

$$\mathcal{E}_{\text{tot}} = \mathcal{E}^{(1)} \otimes \mathcal{E}^{(2)} = \mathcal{E}_{\text{orb}}^{(1)} \otimes \mathcal{E}_{\text{spin}}^{(1)} \otimes \mathcal{E}_{\text{orb}}^{(2)} \otimes \mathcal{E}_{\text{spin}}^{(2)}, \quad (3)$$

where we put labels on the spaces (1 or 2) to indicate which particle they refer to and where in the second form we have broken each single particle Hilbert space into its orbital and spin parts. But since the product of Hilbert spaces such as in Eq. (2) or (3) simply means creating product wave functions by multiplying wave functions from the constituent spaces, we can rearrange the order of the terms in Eq. (3), putting the orbital factors first and the spin factors second,

$$\mathcal{E}_{\text{tot}} = \mathcal{E}_{\text{orb}}^{(1)} \otimes \mathcal{E}_{\text{orb}}^{(2)} \otimes \mathcal{E}_{\text{spin}}^{(1)} \otimes \mathcal{E}_{\text{spin}}^{(2)} = \mathcal{E}_{\text{orb}} \otimes \mathcal{E}_{\text{spin}}, \quad (4)$$

where now \mathcal{E}_{orb} and $\mathcal{E}_{\text{spin}}$ refer to the orbital and spin wave functions in a two-electron system,

$$\mathcal{E}_{\text{orb}} = \mathcal{E}_{\text{orb}}^{(1)} \otimes \mathcal{E}_{\text{orb}}^{(2)}, \quad (5a)$$

$$\mathcal{E}_{\text{spin}} = \mathcal{E}_{\text{spin}}^{(1)} \otimes \mathcal{E}_{\text{spin}}^{(2)} \quad (5b)$$

(not to be confused with \mathcal{E}_{orb} and $\mathcal{E}_{\text{spin}}$ in Eq. (2), which referred to a single particle.)

A basis in the space \mathcal{E}_{orb} in Eq. (5a) is the set of kets $\{|\mathbf{r}_1\mathbf{r}_2\rangle\}$, in terms of which an arbitrary state $|\psi\rangle$ has expansion coefficients $\psi(\mathbf{r}_1, \mathbf{r}_2)$ (a purely spatial wave function for two particles, see Sec. 4.2). Two bases in the space $\mathcal{E}_{\text{spin}}$ in Eq. (5b) are the uncoupled basis $\{|m_1m_2\rangle\}$ and the coupled basis $\{|SM\rangle\}$, related by Eqs. (27.42)–(27.43). See also Sec. 27.8 on the hydrogen molecule.

The equation $\mathcal{E}_{\text{tot}} = \mathcal{E}_{\text{orb}} \otimes \mathcal{E}_{\text{spin}}$ means that an arbitrary state $|\Psi\rangle$ in the two-particle Hilbert space \mathcal{E}_{tot} is a linear combination of products of basis states in \mathcal{E}_{orb} times basis states in $\mathcal{E}_{\text{spin}}$. In general there is no meaning to talking about the “spatial part” or “spin part” of such a state $|\Psi\rangle$. But if $|\Psi\rangle$ should consist of a single state in \mathcal{E}_{orb} times a single state in $\mathcal{E}_{\text{spin}}$, then it does make sense to talk about the “spatial part” or “spin part”. This significance of this discussion for helium is that the energy eigenstates in helium are approximately (but not exactly!) the product of a spatial part times a spin part. That is, the expansion of the exact eigenstates in terms of the product basis is dominated by a single term.

4. Exchange Operators

The Hamiltonian (1) commutes with three exchange operators that we now define, in terms of their action on the basis kets $|\mathbf{r}_1\mathbf{r}_2m_1m_2\rangle$ in \mathcal{E}_{tot} . These are

$$E_{12}^{\text{orb}}|\mathbf{r}_1\mathbf{r}_2m_1m_2\rangle = |\mathbf{r}_2\mathbf{r}_1m_1m_2\rangle, \quad (6)$$

$$E_{12}^{\text{spin}}|\mathbf{r}_1\mathbf{r}_2m_1m_2\rangle = |\mathbf{r}_1\mathbf{r}_2m_2m_1\rangle, \quad (7)$$

$$E_{12}|\mathbf{r}_1\mathbf{r}_2m_1m_2\rangle = |\mathbf{r}_2\mathbf{r}_1m_2m_1\rangle. \quad (8)$$

We will denote the eigenvalues of these three operators by e_{12}^{orb} , e_{12}^{spin} , and e_{12} , respectively.

The Hamiltonian (1) commutes with E_{12}^{orb} because it is a purely orbital operator that is symmetrical in the exchange of the two electrons. It commutes with E_{12}^{spin} because it is a purely orbital

operator that commutes with any spin operator. And since $E_{12} = E_{12}^{\text{orb}} E_{12}^{\text{spin}}$ (see Eq. (9) below), the Hamiltonian (1) commutes with E_{12} .

But the Hamiltonian (1) is only an approximation to the true Hamiltonian for helium. If we include the fine structure terms, which as in hydrogen couple the spin and orbital degrees of freedom, then the resulting Hamiltonian no longer commutes with E_{12}^{orb} or E_{12}^{spin} separately.

It still commutes with E_{12} , however, regardless of how many physical effects we include or how many correction terms we add, because the two electrons are identical. All physical Hamiltonians that describe two electrons commute with E_{12} ; if this were not true, it would be possible to distinguish the electrons.

The properties of these exchange operators follow immediately from their definitions. The operators are all Hermitian and unitary, their square is 1 (the identity operator), and their eigenvalues are ± 1 , as in Eqs. (27.3) and (27.4). They also satisfy

$$E_{12} = E_{12}^{\text{orb}} E_{12}^{\text{spin}}, \quad (9)$$

and

$$[E_{12}^{\text{orb}}, E_{12}^{\text{spin}}] = 0. \quad (10)$$

Thus E_{12}^{orb} and E_{12}^{spin} possess a simultaneous eigenbasis. Since E_{12} is a function of E_{12}^{orb} and E_{12}^{spin} , any simultaneous eigenspaces of E_{12}^{orb} and E_{12}^{spin} is automatically an eigenspace of E_{12} , with eigenvalue

$$e_{12} = e_{12}^{\text{orb}} e_{12}^{\text{spin}}. \quad (11)$$

Not only do E_{12}^{orb} and E_{12}^{spin} commute with each other, but they also commute with the Hamiltonian (1), so all three operators possess a simultaneous eigenbasis. That is, we can find eigenstates of the Hamiltonian (1) that are also eigenstates of E_{12}^{orb} and E_{12}^{spin} . To construct this eigenbasis, we first work on finding the spatial wave functions that are simultaneous eigenfunctions of H and E_{12}^{orb} . Since H is a purely spatial operator, we can view it as an operator acting on wave functions $\psi(\mathbf{r}_1, \mathbf{r}_2)$, that is, we can completely ignore the spin. Let us denote such a wave function in ket language by $|\psi\rangle$, and let us solve the purely spatial eigenvalue-eigenfunction problem,

$$H|\psi\rangle = E|\psi\rangle, \quad (12)$$

using whatever method we can. This is the hard part, and we shall devote some attention to it later. Once this is done, however, we can then construct simultaneous eigenfunctions of H and E_{12}^{orb} by symmetrizing or antisymmetrizing $\psi(\mathbf{r}_1, \mathbf{r}_2)$, if necessary, under exchange of \mathbf{r}_1 and \mathbf{r}_2 . This will not change the energy, that is, the symmetrized or antisymmetrized eigenfunctions will still be energy eigenfunctions. In this way we obtain spatial eigenfunctions that satisfy

$$\psi(\mathbf{r}_2, \mathbf{r}_1) = \pm \psi(\mathbf{r}_1, \mathbf{r}_2), \quad (13)$$

where the ± 1 is the eigenvalue of E_{12}^{orb} , what we have also called e_{12}^{orb} .

Then to create simultaneous eigenstates of all three operators E_{12}^{orb} , E_{12}^{spin} and H (the Hamiltonian (1)), we simply multiply these spatial eigenstates $|\psi\rangle$ of E_{12}^{orb} and H by the spin states $|SM\rangle$, which are antisymmetric under spin exchange when $S = 0$ and symmetric when $S = 1$, as explained in Sec. 27.8. This produces the eigenstates of all three operators, $|\psi\rangle|SM\rangle$.

Finally, in view of Eq. (11), only those states that are symmetric under spatial exchange and antisymmetric under spin exchange, or vice versa, are antisymmetric under total exchange E_{12} , as required by the symmetrization postulate. The physical subspace of the nominal Hilbert space is the direct sum of the subspace with $e_{12}^{\text{orb}} = +1$ and $e_{12}^{\text{spin}} = -1$, and the one with $e_{12}^{\text{orb}} = -1$ and $e_{12}^{\text{spin}} = +1$.

The situation regarding spatial and spin exchange symmetries is summarized in Table 1, which also indicates some standard nomenclature. As in Table 27.1, “para” refers to a wave function that is spatially symmetric, and “ortho” to one that is spatially antisymmetric under exchange. At one time helium was thought to consist of two different species, parahelium and orthohelium, since the spectrum of helium indicates two classes of energy levels with no (or only very weak) transitions between them. Table 1 is almost exactly the same as Table 27.1, the main difference being that in the case of the hydrogen molecule, it was possible to write down an explicit form for the spatial part of the energy eigenfunctions, Eq. (27.33), since we had a central force Hamiltonian, whereas in helium it is much more difficult to solve the spatial eigenfunction equation (12). (And in the hydrogen molecule we had two identical protons, whereas in helium we have two identical electrons.)

e_{12}^{orb}	name	e_{12}^{spin}	e_{12}	S	degen	name
+1	para	-1	-1	0	1	singlet
-1	ortho	+1	-1	1	3	triplet

Table 1. Linkage of spatial and spin exchange symmetry in helium and terminology.

In summary, we have derived the rule about helium eigenfunctions that most students learn in first courses on quantum mechanics, namely, that these eigenfunctions are products of spatial wave functions times spin wave functions with opposite symmetry under exchange. We saw the same rule previously in connection with the hydrogen molecule.

However, the true nature of this rule should be understood. First, the operators E_{12}^{orb} and E_{12}^{spin} do not have the same fundamental significance as the overall exchange operator E_{12} . In particular, there is no symmetrization postulate for E_{12}^{orb} or E_{12}^{spin} . Next, the factorization of the energy eigenfunctions into symmetric spatial parts and antisymmetric spin parts, or vice versa, arises because H commutes with E_{12}^{orb} and E_{12}^{spin} and because commuting operators possess simultaneous eigenstates. If we had included the small fine structure corrections in the Hamiltonian (1), however, then we would find that H no longer commutes with E_{12}^{orb} or E_{12}^{spin} separately, although of course it would still commute with E_{12} . Thus, the usual rule about the factorization of the wave functions only

applies to the nonrelativistic, electrostatic approximation to the helium atom. This is in contrast to the symmetrization postulate itself, which is rigorously correct.

5. Good Quantum Numbers

The helium Hamiltonian (1) is not exactly solvable nor even close to any exactly solvable system (at least for small Z), so it is rather difficult to obtain good approximations to its eigenstates and eigenvalues. In cases like this it is especially important to pay attention to the exact symmetries of the Hamiltonian, that is, the operators that commute with it (the “good quantum numbers”). Commuting operators possess simultaneous eigenbases, and, since symmetry operators are usually easier to diagonalize than Hamiltonians, it is usually a good idea to diagonalize them first. This means that we need only search in the eigenspaces of the symmetry operators for the eigenstates of the Hamiltonian, a significantly easier task than searching in the whole Hilbert space. For example, must diagonalize a matrix to find the energy eigenstates and eigenvalues, it is best to use a symmetry-adapted basis (one that is already an eigenbasis of the symmetry operators). Even if we do not attempt to find the eigenstates of the Hamiltonian explicitly, we can at least say that those eigenstates are labelled by symmetry labels, namely, the quantum numbers of the symmetry operators. This is a common situation for example in particle physics or nuclear physics, where no one knows how to calculate the masses of the baryons or the energies of nuclear states very accurately, but these states are rigorously characterized by their quantum numbers (spin, parity, etc.)

For the helium Hamiltonian (1) we have already begun this process, by noting that H commutes with E_{12}^{orb} and E_{12}^{spin} , and by finding the simultaneous eigenbases of these two operators. This served the dual purpose of narrowing the spaces in which we need to search for energy eigenstates, and of satisfying the symmetrization postulate (by requiring $e_{12} = -1$).

But there are other symmetries of the Hamiltonian (1). Most notably, since H is a scalar operator, it commutes with rotations. In fact, since it is a purely spatial operator, it commutes with both spatial and spin rotations independently, and thus with $\mathbf{L} = \mathbf{L}_1 + \mathbf{L}_2$ and $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$. It does not, however, commute with spatial rotations of particle 1 or of particle 2 separately, because the term $1/r_{12}$ in the Hamiltonian is only invariant when we rotate the positions of both particles simultaneously. That is, H does not commute with \mathbf{L}_1 or \mathbf{L}_2 separately. The Hamiltonian does commute with \mathbf{S}_1 and \mathbf{S}_2 separately, however, in fact, it commutes with any function of spin. But as we have seen, the total spin $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ is more convenient to work with than the individual spins because it is physical and commutes with E_{12}^{spin} , and because the coupled basis is an eigenbasis of E_{12}^{spin} .

The Hamiltonian (1) also commutes with parity π , a purely spatial operator that acts on the basis kets of the entire Hilbert space \mathcal{E} by

$$\pi|\mathbf{r}_1\mathbf{r}_2m_1m_2\rangle = |-\mathbf{r}_1, -\mathbf{r}_2, m_1, m_2\rangle. \quad (14)$$

Parity flips the spatial coordinates of the particles but has no effect on spin (at least in nonrelativistic

quantum mechanics). We will not make much use of parity in the case of helium, but it is more important in multielectron atoms.

Operator	E_{12}^{orb}	E_{12}^{spin}	E_{12}	L^2	L_z	S^2	S_z
Qu. Num.	e_{12}^{orb}	e_{12}^{spin}	$e_{12} = -1$	L	M_L	S	M_S

Table 2. Operators that commute with the approximate helium Hamiltonian (1) and their corresponding quantum numbers. The symmetrization postulate forces $e_{12} = -1$.

A list of operators that H commutes with along with their quantum numbers is shown in Table 2. Moreover these operators commute with each other. Thus, without knowing anything else about the eigenstates of H , we can say that they are characterized by the quantum numbers of the operators in the table. However, several of the quantum numbers are superfluous. For example, e_{12} is forced to be -1 by the symmetrization postulate, so e_{12}^{orb} and e_{12}^{spin} are opposite one another and not independent. In fact, by Eq. (27.44) knowledge of S implies knowledge of e_{12}^{spin} and therefore knowledge of e_{12}^{orb} . Thus an independent set of quantum numbers is (LM_LSM_S) . Within a simultaneous eigenspace of the symmetry operators with the given quantum numbers, we can in principle diagonalize the Hamiltonian, and label the energy eigenstates within that subspace by a sequencing number N . Thus, the energy eigenstates can be denoted $|NLM_LSM_S\rangle$. As for the energy eigenvalues, they are independent of M_L and M_S because of the rotational invariance of the Hamiltonian, so we can write

$$H|NLM_LSM_S\rangle = E_{NLS}|NLM_LSM_S\rangle. \quad (15)$$

The energies E_{NLS} are $(2L+1)(2S+1)$ -fold degenerate, because of the freedom in the magnetic quantum numbers.

You might suspect that the energies E_{NLS} should also be independent of the total spin S , since the Hamiltonian (1) is a purely spatial operator. That would be true if there were no symmetrization postulate, but in that case the quantum number e_{12}^{orb} would not be superfluous, and, since e_{12}^{orb} is a spatial operator itself, the energies would depend on its eigenvalue. In fact, this is precisely what happens in real helium where the symmetrization postulate is operative, it is just that the quantum number e_{12}^{orb} is not explicitly stated since it is determined by the value of S . In other words, in real helium, the spin state specified by S determines the exchange symmetry of the spin part of the wave function which determines the exchange symmetry of the spatial part of the wave function which does affect the energy. Thus, the energy does depend on S , in spite of the fact that H is a purely spatial operator.

In fact, the dependence of the energy on S is typically large, that is, of the order of a Coulomb (electrostatic) energy, much larger than the (magnetic) energies associated with the explicitly spin-dependent terms that we have neglected in Hamiltonian (1). You can see this because wave functions that are symmetric or antisymmetric under spatial exchange have very different distributions of probability in three-dimensional space, and therefore correspond to quite different Coulomb energies. We

will see this explicitly below when we analyze helium by perturbation theory. A similar phenomenon occurs in ferromagnetism, where the energies involved in flipping spins (the magnetization of the material) are much larger than can be accounted for by the magnetic interaction of arrays of magnetic dipoles. This discrepancy in energy scales was known before quantum mechanics had matured, and was regarded as a mystery. The true explanation was given by Heisenberg: when you flip spins, you change the symmetry of the spin part of the wave function, which by the symmetrization postulate forces changes in the spatial part of the wave function, which changes the Coulomb energy of the charge configuration. Ferromagnets are more complicated because there is a large number of particles, but the basic idea is the same as in helium.

In Table 2 we have listed all the obvious symmetries (except parity) of the basic helium Hamiltonian (1). Are there any more (not so obvious) symmetries? Sometimes a system does have additional symmetries in addition to the obvious ones. Notably this happens in the case of hydrogen, which has an $SO(4)$ symmetry (only the $SO(3)$ symmetry under spatial rotations is obvious). This extra symmetry is responsible for the extra degeneracy of hydrogen, in comparison to other central force problems. As we say, hydrogen has “hidden” symmetry. Another example with hidden symmetry is the multidimensional, isotropic harmonic oscillator. Apart from these two examples, however, there are very few systems in the real world with extra or hidden symmetry (it depends partly on your definition of “hidden,” but you should not expect such symmetry in most problems). In particular, helium has no extra symmetry beyond what we have listed.

The standard spectroscopic notation for the level E_{NLS} is $N^{2S+1}L$, where L is replaced by one of the code letters, S, P, D, F , etc., for $L = 0, 1, 2, 3$, etc. Again, capital letters are used to represent the quantum numbers of the whole atom. For example, the state 2^3P is the state with $N = 2$, $S = 1$ and $L = 1$. This is really a manifold of $(2L + 1)(2S + 1) = 3 \times 3 = 9$ degenerate states.

6. Ionization Potentials

So far we have succeeded in labeling the energy levels of helium-like atoms by their good quantum numbers and determining their degeneracies, in the approximation given by Eq. (1), without knowing much about the system apart from its symmetries. We now look at some experimental and other facts about such atoms.

First we present some ionization potentials. The ionization potential of an atom is the energy needed to remove one electron from the atom, assumed to be in its ground state, to infinity. If an atom has several electrons, there are successive ionization potentials, as more and more electrons are removed. The final state consists of a nucleus plus the electrons, all of which are at rest and at an infinite distance from one other.

It is a matter of convention in physics to decide where on the energy axis $E = 0$ lies, since only energy differences are physically meaningful. But it is common in electrostatics to define the state of zero potential energy to be the one in which all charges are at an infinite separation from one another. This is what we have done with the potential energy in the Hamiltonian (1). If the kinetic

energies also vanish, then we have a state of zero total energy. With this convention for the state $E = 0$, the sum of all the ionization potentials of the atom (with a minus sign) is the ground state energy of the atom. (Of course, we don't separate the protons in the nucleus or transport them to infinity. We are using a convention that is convenient in atomic physics, but perhaps not nuclear physics.)

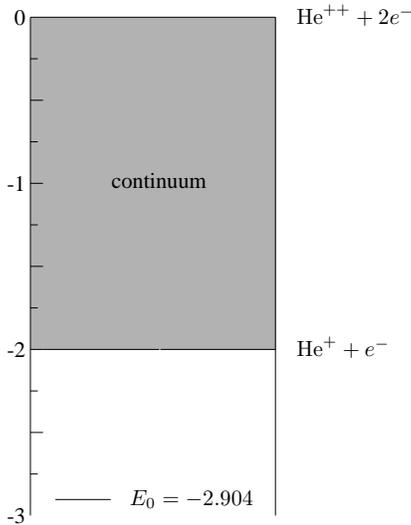


Fig. 1. Important energies of helium obtained from ionization potentials. Energies are measured in atomic units.

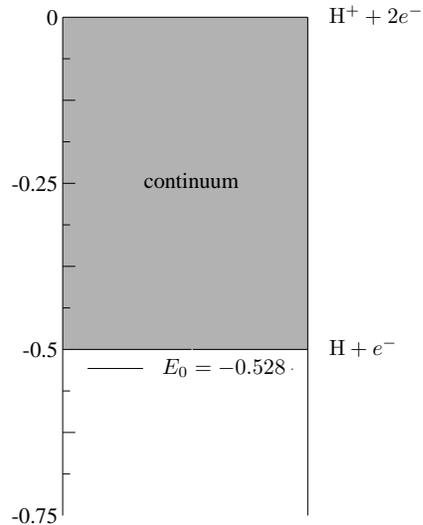


Fig. 2. Same as Fig. 1, but for H^{-} . The energy scale is down by a factor of $1/4$ compared to helium.

In the case of helium, the ionization potentials are

$$\text{He} \rightarrow \text{He}^{+} + e^{-} - 0.904 \text{ a.u.}, \quad (16)$$

$$\text{He}^{+} \rightarrow \text{He}^{++} + e^{-} - 2.0 \text{ a.u.}$$

The first ionization potential may be compared to that of hydrogen, which is 0.5 a.u. In fact, helium has the highest ionization potential of any neutral atom. The second ionization potential is easy to understand, since the He^{+} ion is a hydrogen-like atom, whose ground state energy is $-Z^2/2 = -2 \text{ a.u.}$ To calculate the first ionization potential, however, is a nontrivial problem. In the case of H^{-} , the ionization potentials are

$$H^{-} \rightarrow H + e^{-} - 0.028 \text{ a.u.}, \quad (17)$$

$$H \rightarrow H^{+} + e^{-} - 0.5 \text{ a.u.}$$

In H^{-} the extra electron is only weakly bound to the neutral H atom.

Figures 1 and 2 illustrate the information obtained from the ionization potentials. The energy $E = 0$ is the state of complete dissociation. The ground state energy of helium is $E = -2.904 \text{ a.u.}$, while the state in which one electron has been removed to infinity has energy $E = -2 \text{ a.u.}$ Once this electron has been removed, it may be given any positive kinetic energy, so there is a continuous spectrum above $E = -2 \text{ a.u.}$ In H^{-} , the ground state energy is $E = -0.528 \text{ a.u.}$ and the continuum begins at $E = -0.5 \text{ a.u.}$, the ground state energy of a neutral hydrogen atom.

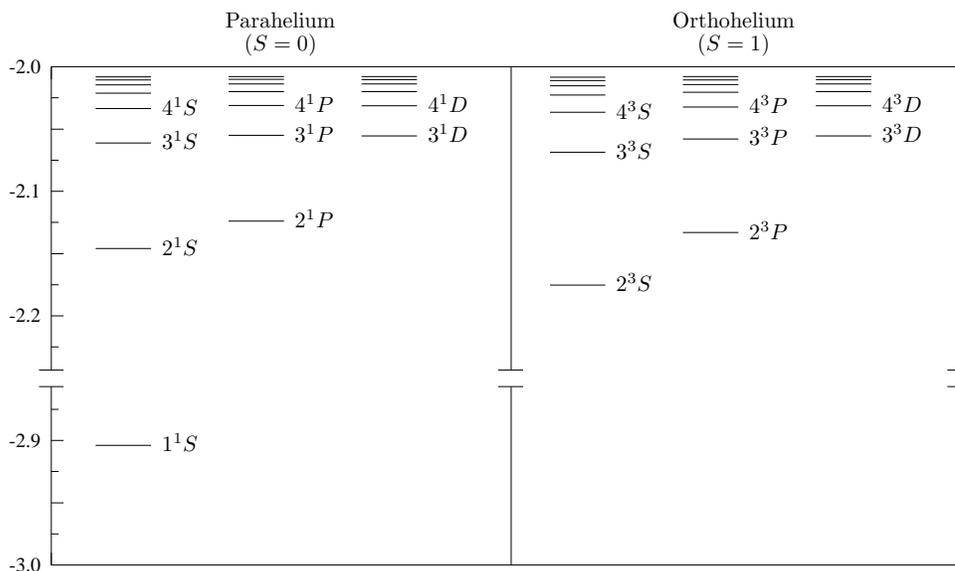


Fig. 3. Bound states of helium with quantum numbers. Energies are measured in atomic units. Notice the gap in the energy scale between the ground state and the excited states.

7. The Bound States

From Fig. 1 it is clear that the bound states of helium must lie between $E_0 = -2.904$ a.u. and $E = -2$ a.u. These bound states and their quantum numbers are displayed in Fig. 3 with an expanded energy scale. The energy levels in the figure are the eigenvalues of the Hamiltonian (1), which are not exactly the same as the experimental values due to the neglect of small terms in that Hamiltonian. The difference, however, is too small to see on the scale of the diagram (in fact, at higher resolution, many of these levels will be seen to have a fine structure splitting).

The levels in Fig. 3 cannot be regarded as purely experimental data, even at a scale where fine structure is ignored and the Hamiltonian (1) is a good approximation, because spectroscopic data only gives differences between energy levels, not their absolute values. It takes some disentangling of the experimental data to produce energy levels. In addition, the levels in Fig. 3 have been assigned quantum numbers, which requires some theoretical input. In effect, we have skipped ahead to the answer (the spectrum of helium) in presenting Fig. 3. This may be the best way to understand helium on a first pass.

In Fig. 3, the para states (spatially symmetric, spin singlet) are on the left, and the ortho states (spatially antisymmetric, spin triplet) are on the right. Each vertical column contains the energy levels for a given value of L and S , the good quantum numbers of the Hamiltonian (1). Only columns out to $L = 2$ (D -states) are shown in the figure, but in actual helium L ranges from 0 to ∞ . The levels in a given column are sequenced in ascending order by N , with certain conventions for the starting value of N . In each column there is an infinite number of levels that accumulate just below the continuum limit, much as in hydrogen. The energy levels in a given column are the eigenvalues of the Hamiltonian (1), restricted to a simultaneous eigenspace of the operators L^2 , S^2 ,

L_z and S_z (it being understood that we are within the antisymmetric eigenspace of the exchange operator E_{12}).

Notice the following qualitative features of the energy level diagram for helium. First, the ground state is a singlet state (1^1S), which is considerably below the excited states (notice the gap in the energy scale). The excited states look roughly the same on the para and ortho sides, but there is no 1^3S state (no state on the ortho side that seems to correspond to the 1^1S state). Second, for a fixed value of N and S , the energies are an increasing function of L (the “staircase effect”) (at least this is true for $N = 2$ and most other values of N). This is the same effect we saw in alkali atoms. Third, for fixed N and L , the ortho states are lower in energy than the para states (thus, if a 1^3S state existed, we would expect it to be below the actual ground state 1^1S). Later we will provide a theoretical explanation for some of these features.

In the case of H^- , the ground state is the only bound state, and it has the quantum numbers 1^1S (same as the ground state of helium).

8. Perturbation Analysis. The Unperturbed System

We now turn to the problem of finding the spatial eigenfunctions of the Hamiltonian (1), which is a purely orbital operator (it does not involve the spin). Denoting such an eigenfunction by $\psi(\mathbf{r}_1, \mathbf{r}_2)$, we wish to solve

$$H\psi(\mathbf{r}_1, \mathbf{r}_2) = E\psi(\mathbf{r}_1, \mathbf{r}_2). \quad (18)$$

In addition, we wish these eigenfunctions to be even or odd under orbital exchange,

$$E_{12}^{\text{orb}}\psi(\mathbf{r}_1, \mathbf{r}_2) = \pm\psi(\mathbf{r}_1, \mathbf{r}_2), \quad (19)$$

where the ± 1 is e_{12}^{orb} , the eigenvalue of E_{12}^{orb} . As explained above, $e_{12}^{\text{orb}} = +1$ are called para states, and $e_{12}^{\text{orb}} = -1$ are called ortho states. We know it is possible to construct simultaneous eigenfunctions of H_0 and E_{12}^{orb} because they commute. Once we have found these eigenfunctions, it will be easy to multiply them by spin states (singlet or triplet) of the opposite exchange symmetry to obtain an overall eigenfunction of the Hamiltonian, including spin, that satisfies the symmetrization postulate. This part is relatively easy; the hard part will be solving Eq. (18) as a purely orbital problem.

An obvious strategy for finding the eigenfunctions of the Hamiltonian (1) is to use perturbation theory, in which the inter-electron Coulomb potential $1/r_{12}$ is taken as a perturbation. That is, we write $H = H_0 + H_1$, where

$$H_0 = \left(\frac{p_1^2}{2} - \frac{Z}{r_1} \right) + \left(\frac{p_2^2}{2} - \frac{Z}{r_2} \right), \quad (20a)$$

$$H_1 = \frac{1}{r_{12}}. \quad (20b)$$

We have grouped the terms in H_0 to emphasize that H_0 is the sum of two hydrogen-like Hamiltonians, one for each electron, moving in the field of a nuclear charge Z . This decomposition of H into H_0

and H_1 is not very favorable for perturbation theory in the case of small Z , since the inter-electron potential is comparable in size to the electron-nucleus potentials. The comparison is especially unfavorable for H^- (the case $Z = 1$). It gets better for larger Z . We do the perturbation analysis anyway, since it is relatively straightforward and there are not many choices.

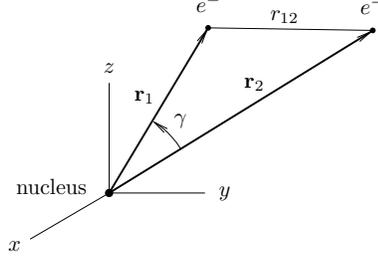


Fig. 4. Coordinates for the nucleus and two electrons in space.

It is obvious from Fig. 4 what the effect of the perturbation $1/r_{12}$ is. When it is switched off, the two electrons no longer repel one another and settle in somewhat closer to the nucleus than they would otherwise. The wave functions for the two electrons can be thought of as two clouds that overlap somewhat in the neighborhood of the nucleus. Conversely, when we turn the perturbation on, the electron clouds expand somewhat so the electrons can get away from one another. They also tend to stay on opposite sides of the nucleus, for the same reason.

As usual in perturbation theory, we must understand the unperturbed system first, its eigenfunctions, degeneracies, and symmetries. Since H_0 is a sum of two hydrogen-like Hamiltonians, the (two-particle) eigenfunctions of H_0 are products of single particle eigenfunctions of the hydrogen-like Hamiltonians in the field of nuclear charge Z . We call these single-particle eigenfunctions *orbitals*. They are central force eigenfunctions, and since we are only concerned with the spatial part here, they are characterized by the usual central force quantum numbers (nlm) . The single particle hydrogen-like energy is $-Z^2/2n^2$. We denote these orbitals in ket language by $|nlm\rangle$. Then the two-particle eigenfunctions of H_0 are products of these, which we denote by

$$|n_1\ell_1m_1\rangle^{(1)}|n_2\ell_2m_2\rangle^{(2)} = |n_1\ell_1m_1 n_2\ell_2m_2\rangle, \quad (21)$$

where the numbers in parentheses indicate which of the two electrons (1 or 2) is referred to, and where the right hand side is a shorthand notation for these states. These states depend on six quantum numbers. They are eigenfunctions of H_0 ,

$$H_0|n_1\ell_1m_1 n_2\ell_2m_2\rangle = E_{n_1n_2}^{(0)}|n_1\ell_1m_1 n_2\ell_2m_2\rangle, \quad (22)$$

where the (0) on the energy indicates that it is the energy in zeroth order of perturbation theory. This zeroth order energy is a sum of the two hydrogen-like energies,

$$E_{n_1n_2}^{(0)} = -\frac{Z^2}{2} \left(\frac{1}{n_1^2} + \frac{1}{n_2^2} \right), \quad (23)$$

and it depends only on the two principal quantum numbers n_1 and n_2 .

The states (21) are eigenstates of H_0 , but not in general of E_{12}^{orb} . However it is easy to construct eigenfunctions of E_{12}^{orb} simply by symmetrizing or antisymmetrizing under exchange. There are two cases. In Case I, the two sets of single particle quantum numbers are equal (all of them), $(n_1 \ell_1 m_1) = (n_2 \ell_2 m_2) \equiv (n \ell m)$, and we write simply

$$|n \ell m n \ell m\rangle \quad (24)$$

for these states. In this case the states are already even under orbital exchange, so they are para states ($e_{12}^{\text{orb}} = +1$). There are no ortho states in Case I.

In Case II, one or more of the two sets of quantum numbers are different, $(n_1 \ell_1 m_1) \neq (n_2 \ell_2 m_2)$. In this case we can easily write down normalized eigenstates of E_{12}^{orb} ,

$$\frac{1}{\sqrt{2}}(|n_1 \ell_1 m_1 n_2 \ell_2 m_2\rangle \pm |n_2 \ell_2 m_2 n_1 \ell_1 m_1\rangle), \quad (25)$$

where the eigenvalue is $e_{12}^{\text{orb}} = \pm 1$. In this case we have both para and ortho states. The energy does not change when we carry out this symmetrization or antisymmetrization because both terms have the same energy. It is still given by Eq. (23), and it does not depend on the choice of the \pm sign. We now have a set of unperturbed energy eigenstates that are also eigenstates of E_{12}^{orb} .

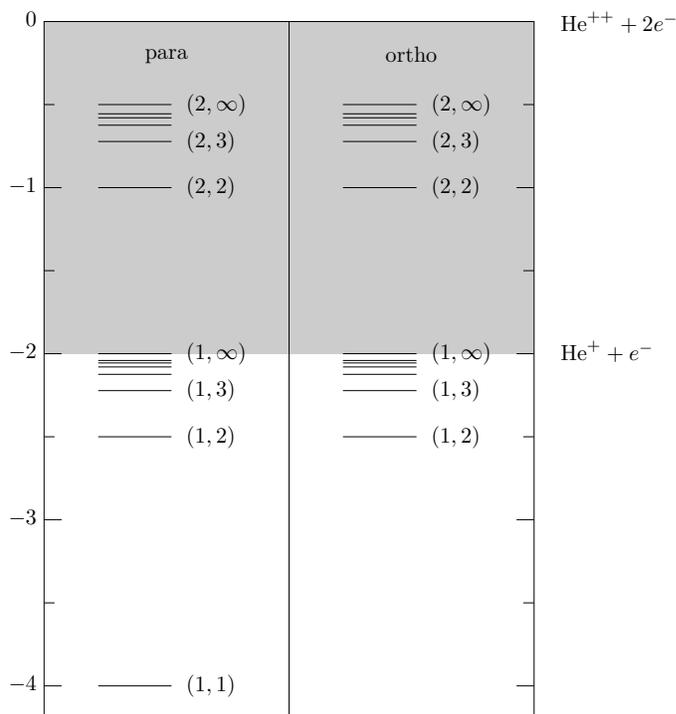


Fig. 5. Unperturbed energy levels of helium, that is, levels of the Hamiltonian (20a). The energy axis is vertical with energies measured in atomic units, and levels are labeled by principal quantum numbers (n_1, n_2) . The shaded area is the continuum.

Figure 5 shows the energy levels of H_0 , with the para states on the left and ortho states on the right. The levels are labeled by their principal quantum numbers (n_1, n_2) .

Let us focus first on the levels below the shaded area in Fig. 5, that is, the levels lying below the continuum threshold at $E = -2$ (all energies are in atomic units). These levels are called *singly excited* states because one of the hydrogen-like orbitals is in the ground state ($n_1 = 1$), while the other (n_2) takes on any value. The absolute ground state of H_0 is the $(1, 1)$ state with $n_1 = n_2 = 1$, at an energy of -4 . The ground state is on the para side; there is no analogous state on the ortho side because this is Case I, described in the paragraph surrounding Eq. (24).

It is instructive to compare these levels with the exact bound states of helium, shown in Fig. 3. One difference is that the levels in Fig. 3 are separated by the L quantum number, while those in Fig. 5 are not. There is no point in separating the levels of Fig. 5 by the orbital angular momentum quantum numbers because the hydrogen-like energies do not depend on them. Apart from that, however, the two energy level diagrams are qualitatively similar. In particular, in both cases we have an infinite number of levels that accumulate at the continuum threshold $E = -2$.

Our analysis of the unperturbed system shows already why there is no 1^3S state in real helium: it is because it would have to be a perturbed version of an antisymmetrized ground state wave function, and the ground state wave function is spatially symmetric. On the other hand, the unperturbed spectrum shows no evidence of the staircase effect (hydrogen energies do not depend on ℓ), and there is exact degeneracy between the ortho and para sides (when a level exists on both sides). That is, the unperturbed energies do not depend on the \pm sign in Eq. (25), which represents the spatial symmetry of the wave function. In addition, the unperturbed ground state is rather badly off in energy, -4 instead of the exact value of -2.904 . In fact, all the unperturbed energies are too low; this is because the perturbation H_1 in Eq. (20b) is a positive operator, and can only raise energies. These differences between the unperturbed and exact spectra are clarified by perturbation theory.

9. The Doubly Excited States

Figure 5 shows something else, the so-called *doubly excited* states in which both orbitals have principal quantum numbers > 1 . The doubly excited series with $n_1 = 2$ and $n_2 \geq 2$ is shown in the figure (twice, once on the para side and once on the ortho side). There are other series (not shown), with $n_1 = 3, 4, \dots$

Insofar as the unperturbed Hamiltonian H_0 is concerned, these are *discrete states imbedded in the continuum*. That is, a state such as the $(2, 2)$ state is a bound state of H_0 with a normalizable wave function, but it exists at an energy that lies in the continuous spectrum of another set of states, those with $n_1 = 1$ and the second electron with a positive energy. The wave functions of the continuum are products of the ground state wave function for the first electron times an unbound hydrogen-like solution for the second electron (subsequently symmetrized or antisymmetrized to obtain a definite exchange symmetry). These wave functions are not normalizable, as we expect in the continuous spectrum.

What happens to these discrete, doubly excited states when the perturbation $1/r_{12}$ is turned on? It turns out that they do not remain discrete states, instead they become coupled to the continuum states of nearby energy, so the actual spectrum of helium above the continuum threshold $E = -2$ is strictly continuous. There are no exact bound states of helium above this energy.

Nevertheless, the exact system does in effect know about the doubly excited states of the unperturbed system. Consider, for example, what happens when we direct a beam of photons of some energy at helium atoms in the ground state. When the photon energy exceeds the ionization potential of helium, 0.904 a.u., it may be absorbed by the atom and an electron ejected. The electron emerges with an energy that is the difference between the photon energy and the ionization potential. One can plot the cross section for this process in this range of energies, and one finds that it has sharp enhancements or peaks at energies that correspond to the doubly excited states. In effect, the photon is raising helium into a doubly excited state, call it He^* , which then decays into He^+ and a free electron. In the future I will locate experimental data on the photoabsorption cross section that shows these features.

This effect can be understood classically. The solar system has eight major planets that move in approximately circular orbits that are stable on human time scales. Nevertheless, it is energetically possible for Jupiter to move somewhat closer to the sun, moving into a lower energy state, and eject all the other seven planets from the solar system. Will this ever happen? Current thinking on this question is that it probably will, if we wait long enough, assuming that the motion of the planets is governed by Newton's laws and no other effects (such as the death of the sun or an encounter with another star) intervene. Nevertheless, the solar system must be mostly stable for very long times, since the earth has apparently been in approximately the same orbit for about 4×10^9 years.

Whether or not the ejection of the major planets is possible, it certainly happens that Jupiter and other planets have encounters with other (usually smaller) objects and cause them to be ejected. This effect is deliberately exploited by spacecraft that are to leave the solar system (such as the Mariner spacecraft).

In the case of the doubly excited states of helium, we can imagine the two electrons having a close encounter, which causes one to drop into the ground state and the other to be ejected. Unlike the case of the solar system, where Jupiter can move into any state of (continuous) lower energy, the first electron must drop into one of the discrete energy levels allowed to it. This is why the actual ground state of helium is stable: the two electrons are interacting strongly all the time, but there are no lower states for one of them to drop into. Apart from the effects of quantization, the classical picture gives an idea of the mechanism in helium. In particular, depending on the two sets of quantum numbers of the doubly excited state, it may take a long time for one electron to have a close encounter with the other. This is like the long-time stability of the solar system. In this case we have a state of the system that is nearly a stationary state, that is, an energy eigenstate. It is not exactly a stationary state, however, instead it is a *resonance*, a state with a finite life time. Resonances were examined in homework problem 7.3 in a simple one-dimensional example.

Helium can be raised into a doubly excited state by many methods, not only absorption of photons but also collisions with electrons or other means. In all cases the double excited state He^* exists for a period of time and then decays into the helium ion He^+ and a free electron. This is called the *Auger process*.

10. Perturbation Analysis of the Ground State

The ground state wave function of H_0 is of the form (24), with $(n\ell m) = (100)$, that is, it is the state $|100\ 100\rangle$. It is nondegenerate, so to compute the energy shift due to H_1 in first order perturbation theory we must compute

$$\Delta E_{\text{gnd}} = \langle 100\ 100 | H_1 | 100\ 100 \rangle = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{|\psi_{100}(\mathbf{r}_1)|^2 |\psi_{100}(\mathbf{r}_2)|^2}{r_{12}}, \quad (26)$$

where we have written out the matrix element explicitly as an integral over the six-dimensional configuration space and where the wave functions are hydrogen-like orbitals in the field of nuclear charge Z .

The integral (26) has an interpretation in electrostatics. The squares of the wave functions seen in that integral are probability densities for the two electrons in physical space, which may be multiplied by the charges $-e = -1$ in atomic units to obtain charge densities. Then the integral is the mutual energy of interaction of the two charge clouds. That is, if we imagine the two charge clouds translated rigidly, starting at an infinite separation, then the integral is the energy required to bring them into their final position where they overlap completely. Because the charge clouds repel one another, this energy is positive. It is precisely the energy shift ΔE in first order perturbation theory.

The hydrogen-like orbital for the ground state is

$$\psi_{100}(\mathbf{r}) = \left(\frac{Z^3}{\pi}\right)^{1/2} e^{-Zr}. \quad (27)$$

To do the integral (26) we expand the Coulomb denominator,

$$\frac{1}{r_{12}} = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} = \sum_{\ell=0}^{\infty} \frac{r_{<}^{\ell}}{r_{>^{\ell+1}}} P_{\ell}(\cos \gamma), \quad (28)$$

where

$$r_{<} = \min(r_1, r_2), \quad r_{>} = \max(r_1, r_2), \quad (29)$$

and

$$\gamma = \angle(\mathbf{r}_1, \mathbf{r}_2). \quad (30)$$

The angle γ is illustrated in Fig. 4. The expansion (28) of the Coulomb denominator (the Green's function for the Poisson equation) is derived in books on electromagnetism, for example, Jackson's. It is very useful in atomic physics. In addition we expand the Legendre polynomial in Eq. (28) in

terms of spherical harmonics, using the addition theorem (15.70). For our present purposes we write this theorem as

$$P_\ell(\cos \gamma) = \frac{4\pi}{2\ell + 1} \sum_m Y_{\ell m}(\Omega_1) Y_{\ell m}^*(\Omega_2). \quad (31)$$

Transforming the integral to spherical coordinates in both \mathbf{r}_1 and \mathbf{r}_2 and collecting all the pieces, we have

$$\begin{aligned} \Delta E_{\text{gnd}} &= \frac{Z^6}{\pi^2} \int_0^\infty r_1^2 dr_1 d\Omega_1 \int_0^\infty r_2^2 dr_2 d\Omega_2 e^{-2Z(r_1+r_2)} \\ &\times \sum_{\ell=0}^\infty \frac{r_{<}^\ell}{r_{>}^{\ell+1}} \frac{4\pi}{2\ell + 1} \sum_m Y_{\ell m}(\Omega_1) Y_{\ell m}^*(\Omega_2) \end{aligned} \quad (32)$$

We do the Ω_2 integral first, using the orthonormality of the $Y_{\ell m}$'s and the fact that $Y_{00} = 1/\sqrt{4\pi}$ is a constant,

$$\int d\Omega_2 Y_{\ell m}^*(\Omega_2) = \sqrt{4\pi} \int d\Omega_2 Y_{\ell m}^*(\Omega_2) Y_{00}(\Omega_2) = \sqrt{4\pi} \delta_{\ell 0} \delta_{m 0}. \quad (33)$$

The Kronecker deltas cause both sums to be replaced by the single term $\ell = m = 0$. Then the Ω_1 integration is easy,

$$\int d\Omega_1 Y_{00}(\Omega_1) = \sqrt{4\pi}. \quad (34)$$

This leaves us with

$$\Delta E_{\text{gnd}} = 16Z^6 \int_0^\infty r_1^2 dr_1 S(r_1), \quad (35)$$

where $S(r_1)$ is the second integral,

$$S(r_1) = \int_0^\infty r_2^2 dr_2 \frac{e^{-2Z(r_1+r_2)}}{r_{>}} = \int_0^{r_1} r_2^2 dr_2 \frac{e^{-2Z(r_1+r_2)}}{r_1} + \int_{r_1}^\infty r_2^2 dr_2 \frac{e^{-2Z(r_1+r_2)}}{r_2}. \quad (36)$$

These integrals are elementary and after some algebra we find

$$\Delta E_{\text{gnd}} = \frac{5}{8}Z, \quad (37)$$

or

$$E_{\text{gnd}}^{(1)} = -Z^2 + \frac{5}{8}Z, \quad (38)$$

where the (1) means the energy correct to first order of perturbation theory. Evidently perturbation theory is developing a series in inverse powers of Z .

Atom	Z	$E_{\text{gnd}}^{(0)}$	$E_{\text{gnd}}^{(1)}$	$E_{\text{gnd}}^{\text{exact}}$
H ⁻	1	-1	-0.375	-0.528
He	2	-4	-2.75	-2.904

Table 3. Comparison of ground state energies at zeroth and first order of perturbation theory with the exact ground state energies, for H⁻ and He.

Table 3 shows a numerical comparison of the ground state energies of helium, as estimated from the unperturbed system and from first order perturbation theory, in the case of He and H^- . It will be seen that the first order correction does close the gap between the calculated energy and the true energy, but it overshoots the mark and ends up being too high. If we knew nothing about the exact ground state energy, then based on our calculation we would have no knowledge of whether our first order estimate was too high or too low. Notice that the first order estimate for the ground state energy of H^- is above the continuum threshold of $E = -0.5$. But given our lack of knowledge about the magnitude or even the sign of the error, this gives us no information about whether H^- exists as a bound state. The variational principle does better in this regard.

Problems

1. The bound states of helium are shown in Fig. 3.

(a) How would this diagram be different if the electron were a spin 0 particle? If it were a spin $\frac{3}{2}$ particle? You do not need to be quantitative, but if some levels go up or down, say which ones and which way. If some levels appear or disappear, say which ones. What are the degeneracies of the levels in actual helium? What would they be if the electron were a spin-0 particle?

(b) The electric dipole operator for a multielectron atom is defined by Eq. (22.15), where the charges are the electrons (with $q = -e$). Electric dipole transitions between two states are governed by the matrix element of the electric dipole operator between the states in question. Explain why there are no electric dipole transitions between ortho and para eigenstates of the Hamiltonian (1).

Remark: The eigenstates of the Hamiltonian (1) are not exactly the eigenstates of real helium because of the neglect of small terms, notably, the fine structure terms. When these are included, it turns out that electric dipole transitions are allowed between ortho and para states, but the amplitude is small and the lines are very weak. For this reason, it was thought at one time on spectroscopic grounds that parahelium and orthohelium were two different species of helium. The weak spectral lines connecting the ortho and para states are called “intercombination lines.”

2. This problem was borrowed from Eugene Commins. Consider a simple “one-dimensional” hydrogen atom that obeys the equation,

$$-\frac{1}{2} \frac{\partial^2 \psi}{\partial x^2} - Z\delta(x)\psi = E\psi. \quad (39)$$

[Units such that $m = \hbar = 1$, and the Coulomb potential is replaced by $-Z\delta(x)$].

(a) Find the ground state energy and wave function $\psi_0(x)$, and verify that

$$\langle T \rangle = -E = -\frac{1}{2} \langle V \rangle. \quad (40)$$

(b) Now consider the one-dimensional “helium” atom which obeys

$$H\psi(x_1, x_2) = -\frac{1}{2}\frac{\partial^2\psi}{\partial x_1^2} - \frac{1}{2}\frac{\partial^2\psi}{\partial x_2^2} - Z\delta(x_1)\psi - Z\delta(x_2)\psi + \delta(x_1 - x_2)\psi = E\psi, \quad (41)$$

where x_1, x_2 are the coordinates of the two “electrons” on the x -axis. First treat $\delta(x_1 - x_2)$ as a perturbation and find the ground state energy to first order. Compare to 3-dimensional helium.

(c) Now employ the variational method with a trial wave function analogous to that used in class for the ground state of 3-dimensional helium. Find the best value of $\langle H \rangle$ and compare to 3-dimensional helium.

(d) For one-dimensional “helium,” take a trial wave function of the form

$$\psi(x_1, x_2) = u(x_1)u(x_2), \quad (42)$$

where $u(x)$ is the variational parameter (that is, the whole function, as in Hartree theory). Assume $u(x)$ is real; there is no loss of generality in this. Find an equation for $u(x)$. It will be a kind of Hartree equation, and it will contain a pseudo-energy eigenvalue, call it ϵ . Define ϵ so that the equation looks like

$$-\frac{1}{2}u''(x) + \dots = \epsilon u(x), \quad (43)$$

where the ellipsis indicates omitted terms.

(e) The desired solution must be normalizable (in fact, we demand that it be normalized), so we must have

$$\lim_{x \rightarrow \pm\infty} u(x) = 0. \quad (44)$$

Show that this can only be satisfied if $\epsilon < 0$. Hint: To solve the equation, make the change of notation, $u \rightarrow x, x \rightarrow t$, and interpret it as a one-dimensional problem in classical mechanics.

(f) Find the normalized solution $u(x)$ and the pseudo-eigenvalue ϵ .

(g) Find the variational estimate of the ground state energy of one-dimensional “helium”. Hint: Note that

$$\langle H \rangle = 2\epsilon - \langle \delta(x_1 - x_2) \rangle. \quad (45)$$

Does your new estimate improve on the results of part (a)? Would you expect it to do so?

3. For this problem you should review the lecture notes on the perturbation theory for the excited states of helium, in which the energy shifts were shown to be of the form $J_{n\ell} \pm K_{n\ell}$.

(a) The exchange integral $K_{n\ell}$ defined in lecture and in the lecture notes depends on two hydrogen-like orbitals. It is easily generalized to any two single-particle orbitals (recall that “orbital” means a single-particle wave function). Show that if the two orbitals have no spatial overlap, then the

exchange integral vanishes. Then use your knowledge of hydrogen-like orbitals to explain the dependence of the exchange integral on n for fixed ℓ , and on ℓ for fixed n . This has certain implications for the energy levels of the excited states of helium.

(b) Go to http://physics.nist.gov/PhysRefData/ASD/levels_form.html and check your predictions using the experimental data on the first several excited states of helium. Enter “He I” for the atom (this is neutral helium). You will see that some of the levels have a fine structure, which we did not discuss in detail in class. This should not prevent you from checking your predictions.