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Hydrogenic Atoms in a Magnetic Field

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The interaction of hydrogenic atoms with a weak constant magnetic field is discussed in detail. The Breit Hamiltonian, minimally coupled to the external magnetic field, is treated in several different ways. First, approximate eigenfunctions are obtained in the nonrelativistic nucleus approximation. These wave functions are used to treat perturbatively the residual terms dependent on the magnetic field, and to identify the magnetic moment of the bound electron in the ground state. The corrections previously given by us, of relative order $(Z\alpha)^2$, $(Z\alpha)^2 m/M$, $\alpha(Z\alpha)^2$, and $\alpha(Z\alpha)^2 m/M$, are confirmed including lowest-order radiative corrections. Next, a unitary transformation of the complete Breit Hamiltonian is made in order to simplify further the calculation of small corrections to the electron and nuclear g factors. The physical origin of this unitary transformation, which is similar to a gauge transformation, is discussed extensively, and it is shown that the transformed Hamiltonian for a neutral system commutes with $\vec{P}$, the momentum conjugate to the center-of-mass position $\vec{X}$. This new Hamiltonian, which treats the electron and the nucleus on equal footing, is then transformed by means of the Chraplyvy-Barker-Glover reduction. The electron and the nuclear g factors are calculated, this time including terms of relative order $(Z\alpha)^2 m^2/M^2$ and $\alpha(Z\alpha)^2 m^2/M^2$. These computations yield the magnetic moments for hydrogenic atoms in their ground state. The theoretical results are summarized and compared with recent experiments.

I. INTRODUCTION

Recent work in the precision atomic spectroscopy of simple atoms indicates a need for greater accuracy in the theoretical calculations of the external electromagnetic interactions of composite systems.[1] Although, in principle, it is not difficult to achieve such accuracy, in practice there are some problems to surmount; these will be discussed below.

A bound state such as hydrogen is properly described by the Bethe-Salpeter (BS) equation.[2] The advantage of this approach is that it is fully covariant and it treats the electron and the proton on an equal footing. The interaction between them is prescribed by the irreducible Feynman graphs which provide the interaction kernel. If the atom is in an external field, the BS equation may be minimally coupled provided the external field is time independent.

The BS approach is a two-time formalism, but under certain approximations it is possible to derive from it a single-time formalism. Examples are provided by the Schrödinger equation, the Dirac equation, the Breit equation, and the Salpeter equation. In the present paper the Breit equation will be used to study hydrogenic atoms.

The Breit equation is an approximate two-body formalism which provides a suitable starting point for consideration of atomic problems. Its deficiencies are well understood and do not affect the considerations of this paper. In a sense the Breit equation is often a better starting point for consideration of atomic problems than is the BS equation in ladder approximation, for while the former reduces to the Dirac equation in the limit of infinite nuclear mass, the latter does not. It is known that in the BS formalism crossed graphs must be included to recover the Dirac equation.[3]

To obtain the energy levels of the isolated atom it is sufficient to solve the eigenvalue problem in the center-of-mass (c.m.) frame. However, if the atom is interacting with an external field, the atomic momentum can change and therefore perturbative methods require a knowledge of the full wave function, and not merely the c.m. wave function. In nonrelativistic quantum mechanics, the separability of the Schrödinger Hamiltonian of the isolated atom into conventional c.m. and relative variables guarantees that the total atomic wave function is known once the c.m. wave function is known. Relativistic Hamiltonians such as the Breit Hamiltonian are not separable in the above sense and therefore the problem of determining the complete wave function is nontrivial. This nonseparability is the basic problem which must be surmounted in order to handle the problem of electromagnetic interactions. Recently a number of papers have considered the electromagnetic interactions of loosely bound systems by various methods.[4-7] The present paper suggests another approach but considers in detail only the interaction of hydrogenic atoms in a magnetic field. It contains a more comprehensive treatment of work previously discussed more briefly by both authors.

In Sec. II we show that approximate solutions of the Breit equation may be obtained to describe the motion of the atom. We discuss the approximate nature of these solutions. In Sec. III we treat the important problem of the hydrogenic atom in an external magnetic field. Only the ground state is discussed here although in future work it should be easy to analyze excited states. We calculate bound-state corrections to the electron g factor including terms of order $(Z\alpha)^2 m/M$. Section III, as well as Sec. IV, in which the radiative corrections are analyzed, gives a detailed treatment of earlier work published by one of us (H.G.).[8] Since the wave functions are not accurate enough to calculate the corrections of order $(Z\alpha)^2 m^2/M^2$, further accuracy is achieved by using the Barker-Glover method, the approach previously discussed by one of us (R.A.H.).[9] In Sec. V we discuss a unitary transformation of the Hamiltonian which greatly simplifies the calculations. This Hamiltonian also includes the anomalous moment terms discussed earlier. In Sec. VI the Barker-Glover method is used to transform the Hamiltonian of Sec. V to a form in which the operators are even (with respect to Dirac matrices) in both electron and nuclear variables. Both the electron and the proton g factors are obtained for the 1S state of hydrogen. Finally, in Sec. VII we summarize the results and make some comparisons with experiment.

II. APPROXIMATE SOLUTION OF BREIT EQUATION

The Breit equation provides an approximate treatment of the two-body problem.[10] Its deficiencies are understood and it is known that certain recoil corrections to fine structure and hyperfine structure are not contained in this formalism.[11] Nevertheless, for our purposes the Breit equation with Coulomb and Breit potentials is sufficiently accurate.

The Hamiltonian is

$$H_0 = \vec{\alpha}_e \cdot \vec{p}_e + \beta_e m + \vec{\alpha}_p \cdot \vec{p}_p + \beta_p M - Z\alpha/r + (Z\alpha/2r)(\vec{\alpha}_e \cdot \vec{\alpha}_p + \vec{\alpha}_e \cdot \hat{r}\vec{\alpha}_p \cdot \hat{r}), \qquad (1)$$

where variables subscripted with e or p denote electron and nuclear variables, and Z is the nuclear charge.

In working with this Hamiltonian we must keep in perspective its approximate nature. Consistency requires that in applications the Breit potential should only be treated in first order, since second-order effects would give results of the same order as terms which have been neglected in Eq. (1).

Keeping this limitation in mind, we may derive from Eq. (1) a Hamiltonian H which acts only in the upper component space of the nucleus. In effect we are treating the nucleus as nonrelativistic. This approximation is valid in most hydrogenic atoms (positronium excluded) because of the smallness of the ratio m/M.

Dropping nuclear-spin-dependent terms, which may be handled by perturbation theory, we obtain to first order in M^{-1}

$$H = \vec{\alpha}_e \cdot \vec{p}_e + \beta_e m + M + \vec{p}_p^{\,2}/2M - Z\alpha/r + (Z\alpha/2Mr)(\vec{\alpha}_e \cdot \vec{p}_p + \vec{\alpha}_e \cdot \hat{r}\,\hat{r} \cdot \vec{p}_p) \,. \qquad (2)$$

This is exactly the Hamiltonian given by Grotch and Yennie from the effective-potential viewpoint.[12] It is also the Hamiltonian which replaces Eq. (1) when the nucleus is spinless.

The electron and the nuclear variables in Eq. (2) may be written in terms of relative and c.m. variables, using $\vec{p}_e = \vec{p} + [m/(m+M)]\vec{P}$, $\vec{p}_p = -\vec{p} + [M/(m+M)]\vec{P}$, $\vec{x}_e = \vec{X} + [M/(m+M)]\vec{r}$, and $\vec{x}_p = \vec{X} - [m/(m+M)]\vec{r}$. H may then be written as

$$\begin{aligned} H = {} & \vec{\alpha}_e \cdot \vec{p} + \beta_e m + M + \frac{\vec{p}^{\,2}}{2M} - \frac{Z\alpha}{r} - \frac{Z\alpha}{2Mr}(\vec{\alpha}_e \cdot \vec{p} + \vec{\alpha}_e \cdot \hat{r}\,\hat{r} \cdot \vec{p}) + \frac{m}{m+M}\,\vec{\alpha}_e \cdot \vec{P} \\ & - \frac{\vec{p} \cdot \vec{P}}{m+M} + \left(\frac{M}{m+M}\right)\frac{\vec{P}^{2}}{2(m+M)} + \frac{Z\alpha}{2r(m+M)} \\ & \times (\vec{\alpha}_e \cdot \vec{P} + \vec{\alpha}_e \cdot \hat{r}\,\hat{r} \cdot \vec{P}) \equiv H_{\text{rel}} + H_P \,, \end{aligned} \qquad (3)$$

where H_{rel} contains only relative variables and H_P contains all $\vec{P}$-dependent terms.

Approximate eigenfunctions of H_{rel} have been given in Ref. 12. In obtaining these, H_{rel} was rearranged and approximated by discarding some operators of order $(m/M^2)(Z\alpha/r)^2$ and $(m/M^2)\vec{\alpha} \cdot \vec{p}\,Z\alpha/r$. Therefore, in doing computations with these wave functions, errors of relative order $(Z\alpha)^2 m^2/M^2$ are possible.

Let $\psi_0(\vec{r})$ be the approximate eigenfunction of H_{rel} with eigenvalue $\mathfrak{M}$, where $\mathfrak{M}$ is equal to $m + M + \epsilon$, ϵ being the binding energy. In the Appendix we show that

$$\psi_K(\vec{r},\vec{X}) = (1+\vec{\alpha}_e\cdot\vec{K}/2\mathfrak{M} + i\eta\vec{r}\cdot\vec{K}/\mathfrak{M})\,\psi_0(\vec{r})\,e^{i\vec{K}\cdot\vec{X}} \tag{4}$$

is an approximate eigenfunction of H, characterizing an atom of momentum $\vec{K}$, where $\eta=\epsilon+Z\alpha/2r$. In proving this we have ignored certain terms of order $mK\epsilon/M^2$ and $K^2\epsilon/M^2$, and therefore in Eq. (4) the term $i\eta\vec{r}\cdot\vec{K}/\mathfrak{M}$ could just as well be replaced by $i\eta\vec{r}\cdot\vec{K}/M$. Moreover, the energy eigenvalue corresponding to Eq. (4) is $\mathfrak{M}+\vec{K}^2/2\mathfrak{M}$. However, $\vec{K}^2/2\mathfrak{M}$ could just as well be $\vec{K}^2/2(m+M)$ since our approximations are not accurate enough to obtain the exact kinetic-energy term $\vec{K}^2/2\mathfrak{M}$.

Recently Brodsky and Primack[4] have given a solution of the Breit equation which also includes c.m. motion. We would like to compare and contrast their result with Eq. (4). The approach of the present work has been to assume the validity (approximate) of the Breit equation in the laboratory frame and to separate the interaction into an instantaneous and a transverse part in that frame. The Hamiltonian is not separable in conventional relative and c.m. variables as in the nonrelativistic case. However, it is possible to obtain the wave function for the slowly moving atom once the wave function $\psi_0(\vec{r})$ of the stationary atom is known.

Brodsky and Primack[4] assume a Breit equation in the c.m. frame of the atom, and that the interaction separates into a Coulomb and Breit part (they drop the Breit part since their work does not require it). At this stage, a single-time formalism exists in the c.m. frame. The wave function for the moving atom is obtained by performing appropriate Lorentz boosts of the c.m. wave function.[13] This procedure is perfectly natural, but it should be remembered that the boosted solution is actually a solution of the BS equation in the laboratory frame. This solution is a two-time wave function and, moreover, it satisfies a BS equation in which the gauge is no longer the Coulomb gauge and the interaction is no longer instantaneous.

Using our approach, the electromagnetic interactions of a composite system are described by minimally coupling the Breit equation in the laboratory frame, whereas in the approach of Ref. 4 the BS equation in the lab frame corresponding to the assumed c.m. conditions must be minimally coupled.[14] For the work described in this paper we prefer the former method, although the latter method would appear to be advantageous in its handling of covariance.

III. MAGNETIC INTERACTIONS OF HYDROGENIC ATOMS

When a constant magnetic field $\vec{H}$ is applied, the Hamiltonian of Eq. (1) is modified through the replacement of $\vec{p}_e$ and $\vec{p}_p$, respectively, by $\vec{p}_e - e\vec{A}_e$ and $\vec{p}_p + Ze\vec{A}_p$, where $\vec{A}_{e,p}=\frac{1}{2}\vec{H}\times\vec{x}_{e,p}$. This minimal coupling procedure will also change the Hamiltonian H of Eq. (2), the change being effected by the same replacements.

If we retain only terms linear in $\vec{H}$ (quadratic terms are only needed for large fields), we obtain an addition to Eq. (2) given by H_{mag}, where

$$\begin{aligned} H_{\text{mag}} = {} & -e\vec{\alpha}_e\cdot\vec{A}_e + (Ze/M)\,\vec{p}_p\cdot\vec{A}_p \\ & + (Z^2\alpha e/2Mr)\,(\vec{\alpha}_e\cdot\vec{A}_p + \vec{\alpha}_e\cdot\hat{r}\;\hat{r}\cdot\vec{A}_p)\;. \end{aligned} \tag{5}$$

The change in the energy levels due to H_{mag} may be evaluated by means of first-order perturbation theory, using the wave functions of Eq. (4). It is important to note, however, that $[\vec{P}, H_{\text{mag}}]\neq 0$ and therefore $\vec{P}$ is not a conserved quantity. This raises doubts concerning the validity of the use of nondegenerate perturbation theory (e.g., for s states) since there is a great deal of degeneracy due to the continuum of unperturbed eigenstates of $\vec{P}$, all having the same energy. However, it turns out that for a constant magnetic field, spin-dependent terms are diagonal between eigenstates of $\vec{P}$ and therefore questions of degeneracy do not arise.[15]

To evaluate the matrix elements of H_{mag} we first evaluate

$$\left(1+\frac{\vec{\alpha}_e\cdot\vec{P}}{2M}-\frac{i\eta\vec{r}\cdot\vec{P}}{M}\right)H_{\text{mag}}\left(1+\frac{\vec{\alpha}_e\cdot\vec{P}}{2M}+\frac{i\eta\vec{r}\cdot\vec{P}}{M}\right) \tag{6}$$

to order M^{-1}. Thereafter the expression of Eq. (6) is to be evaluated using wave functions $\psi_0(\vec{r})e^{i\vec{K}\cdot\vec{X}}$. We obtain from Eq. (6)

$$\begin{aligned} & -e\vec{\alpha}_e\cdot\vec{A}_e + \frac{Ze}{M}\,\vec{p}_p\cdot\vec{A}_p + \frac{Z^2\alpha e}{2Mr}\,(\vec{\alpha}_e\cdot\vec{A}_p + \vec{\alpha}_e\cdot\hat{r}\;\hat{r}\cdot\vec{A}_p) \\ & \qquad - \frac{e}{M}\,\vec{P}\cdot\vec{A}_e - \frac{e}{2M}\,\vec{\sigma}_e\cdot\vec{H} + \frac{e}{2M}\,\eta\vec{\alpha}_e\cdot\vec{H}\times\vec{r}\;. \end{aligned} \tag{7}$$

At this point we separate Eq. (7) into relative and c.m. coordinates to obtain to order M^{-1}

$$\begin{aligned} & -e\vec{\alpha}_e\cdot\tfrac{1}{2}\vec{H}\times\vec{r}\left(1-\frac{m}{M}\right) - \frac{e}{2M}\,\vec{\sigma}_e\cdot\vec{H} + \frac{e}{2M}\,\eta\vec{\alpha}_e\cdot\vec{H}\times\vec{r} \\ & -e\vec{\alpha}_e\cdot\tfrac{1}{2}\vec{H}\times\vec{X} - \frac{Ze}{M}\,\vec{p}\cdot\tfrac{1}{2}\vec{H}\times\vec{X} + \frac{(Z-1)e}{M}\,\vec{P}\cdot\tfrac{1}{2}\vec{H}\times\vec{X} \\ & -\frac{e}{M}\,\vec{P}\cdot\tfrac{1}{2}\vec{H}\times\vec{r} + \frac{Z^2\alpha e}{2Mr}\,(\vec{\alpha}_e\cdot\tfrac{1}{2}\vec{H}\times\vec{X} + \vec{\alpha}_e\cdot\hat{r}\;\hat{r}\cdot\tfrac{1}{2}\vec{H}\times\vec{X}). \end{aligned} \tag{8}$$

For comparison with previous work[16] we examine the terms containing c.m. variables in the limit of ignoring the binding-energy corrections. When $-e\vec{\alpha}_e\cdot\frac{1}{2}\vec{H}\times\vec{X}$ is taken between the relative wave functions, it contributes $-(e/m)\vec{p}\cdot\frac{1}{2}\vec{H}\times\vec{X}$, and therefore the c.m. terms become

$$\begin{aligned} & (-e/m - Ze/M)\,\vec{p}\cdot\tfrac{1}{2}\vec{H}\times\vec{X} + [(Z-1)e/M]\,\vec{P}\cdot\tfrac{1}{2}\vec{H}\times\vec{X} \\ & \qquad - (e/M)\,\vec{P}\cdot\tfrac{1}{2}\vec{H}\times\vec{r}\;, \end{aligned} \tag{9}$$

a result in agreement with Ref. 16. Of course, there are also binding corrections to this result but these are not of interest here.

The first three terms of Eq. (8) affect the energy levels of a stationary atom and therefore give rise to the customary Zeeman effect. Using this interaction, we may calculate the electron g factor for various states. Our main interest is in computing the order $(Z\alpha)^2 m/M$ correction to the g factor in the ground state, although similar corrections may also be calculated for excited states but are probably of little importance since precision experiments are not accurate enough for these states.

The relative wave function of Eq. (4) may be taken from Ref. 12. To the required accuracy[17]

$$\psi_0(\vec{r}) = \left[1 - \frac{Z\alpha}{2M}\left(\frac{1}{r} + i\,\frac{\vec{r}}{r}\cdot\vec{p}\right)\right]\frac{1+\beta\lambda}{1+\lambda}\,\phi_0(\vec{r})$$

and (10)

$$\psi_0^\dagger(\vec{r}) = \phi_0^\dagger(\vec{r})\,\frac{1+\beta\lambda}{1+\lambda}\left[1 + \frac{Z\alpha}{2M}\left(\frac{1}{r} + i\,\frac{\vec{r}}{r}\cdot\vec{p}\right)\right],$$

where $\lambda = \frac{1}{2}m/M$ and $\phi_0(\vec{r})$ is the Dirac wave function for the Coulomb problem with a modified mass $m' \simeq m(1 - m/M)$ and a modified fine-structure constant $\alpha' = \alpha/(1 - m^2/M^2)^{1/2}$.

We then obtain

$$\left\langle \frac{-1}{(1+\lambda)^2}\, e\vec{\alpha}_e\cdot\tfrac{1}{2}\vec{H}\times\vec{r}\left(1 - \frac{m}{M} - \frac{1}{M}\eta\right) - \frac{e}{2M}\,\vec{\sigma}_e\cdot\vec{H} - \frac{e}{2M}\,\frac{Z\alpha}{r}\,\vec{\alpha}_e\cdot\tfrac{1}{2}\vec{H}\times\vec{r}\right\rangle, \quad (11)$$

where now the matrix element is taken with the Dirac wave function $\phi_0(\vec{r})$. The last term of Eq. (11) comes from the $-(Z\alpha/2M)i\,(\vec{r}/r)\cdot\vec{p}$ term in Eq. (10). It cancels part of the η contained in the first term so that finally we obtain

$$\left\langle \frac{-1}{1+m/M}\, e\vec{\alpha}_e\cdot\tfrac{1}{2}\vec{H}\times\vec{r}\left(1 - \frac{m}{M} - \frac{1}{M}\epsilon\right) - \frac{e}{2M}\,\vec{\sigma}_e\cdot\vec{H}\right\rangle. \quad (12)$$

This is easily evaluated in the ground state to obtain

$$\left\langle -\frac{e}{2m}\,\vec{\sigma}_e\cdot\vec{H}\left[1 - \tfrac{1}{3}(Z\alpha)^2\right]\left(1 - \frac{m}{M} - \frac{1}{M}\epsilon\right) - \frac{e}{2M}\,\vec{\sigma}_e\cdot\vec{H}\left[1 - \tfrac{1}{3}(Z\alpha)^2\right]\right\rangle, \quad (13)$$

where now the matrix element is taken between two-component spinors. The final result is

$$\langle -(e/2m)\,\vec{\sigma}_e\cdot\vec{H}\left[1 - \tfrac{1}{3}(Z\alpha)^2 + \tfrac{1}{2}(Z\alpha)^2 m/M\right]\rangle. \quad (14)$$

The g factor (excluding radiative corrections) of the bound electron is therefore $2[1 - \frac{1}{3}(Z\alpha)^2 + \frac{1}{2}(Z\alpha)^2 m/M]$, a result which one of us has presented elsewhere in a more succinct paper.[8(b)]

Orbital g factors may also be calculated from Eq. (11) for various excited atomic states. The results of order $(Z\alpha)^2$ agree with those of Ref. 16, while those of order $(Z\alpha)^2 m/M$ are not likely to be of interest.

We wish to stress the importance, in the above calculation, of the c.m. dependence in the wave function. This has been discussed earlier.[8] If one assumes the atom to be at rest from the start, then certain terms in Eq. (8) arising from commutators of $\vec{X}$ and $\vec{P}$ will be missing and will cause an error in the g factor of order $\alpha^2 m/M$. In Sec. V we discuss a unitary transformation which eliminates to a large degree the complication of c.m. motion and thus makes the problem substantially easier to solve.

IV. RADIATIVE CORRECTIONS

Thus far we have not considered the interactions due to radiative effects. The radiative corrections modify the magnetic moments of the free particles and also add to the binding corrections to the g factors. In the present section we are interested in the electron g factor (and not the nuclear g factor) and therefore we consider the electron as being bound to a scalar nucleus. Nuclear spin will be discussed in Sec. VI.

As discussed in Ref. 8(a), the corrections due to lowest-order radiative processes should come from self-energy modifications of the propagator of the bound electron as well as from vacuum polarization corrections to the photon propagator.

Brodsky and Erickson[18] have developed a formalism for handling such radiative level shifts. Careful examination of all possible contributions indicates that only the terms considered here can be important when working to first order in binding corrections.

For the level shift due to the self energy correction we obtain

$$\Delta E(M) = -(e/2m)\;(\alpha/2\pi)\langle\beta_e\vec{\sigma}_e\cdot\vec{H}_e - i\vec{\gamma}_e - \vec{E}_e\rangle, \quad (15)$$

where $\vec{H}_e$ and $\vec{E}_e$ are the total magnetic and electric fields at the electron. In the present case, $\vec{H}_e$ is approximately the external magnetic field and $\vec{E}_e$ is the Coulomb field. In other words, to first order the level shift is given by the expectation value of the Pauli interaction in the field discussed above.

To evaluate Eq. (15), we first compute

$$-\frac{e}{2m}\,\frac{\alpha}{2\pi}\left(1 + \frac{\vec{\alpha}_e\cdot\vec{P}}{2M} - \frac{i\eta\vec{r}\cdot\vec{P}}{M}\right)(\beta_e\vec{\sigma}_e\cdot\vec{H} - i\vec{\gamma}_e\cdot\vec{E}_e) \times\left(1 + \frac{\vec{\alpha}_e\cdot\vec{P}}{2M} + \frac{i\eta\vec{r}\cdot\vec{P}}{M}\right) \quad (16)$$

to order M^{-1} and then use wave functions as discussed below Eq. (6). This gives the result

$$-\frac{e}{2m}\,\frac{\alpha}{2\pi}\left[\beta_e\vec{\sigma}_e\cdot\left(\vec{\mathrm{H}}-\frac{\vec{\mathrm{P}}}{M}\times\vec{\mathrm{E}}_e\right)-i\vec{\gamma}_e\cdot\left(\vec{\mathrm{E}}_e+\frac{\vec{\mathrm{P}}}{M}\times\vec{\mathrm{H}}\right)\right]\,, \tag{17}$$

which explicitly demonstrates the interactions with motional electric and magnetic fields.

Consider now nonmotional terms, the largest of these being $\beta_e\vec{\sigma}_e\cdot\vec{\mathrm{H}}$. In evaluating this term using the relative wave function, it is necessary to include both the upper and lower components of the wave function and to note that the upper components are not normalized to unity. The result from this term will be (for the ground state or other S states)

$$-(e/2m)(\alpha/2\pi)\langle\vec{\sigma}_e\cdot\vec{\mathrm{H}}\,(1-\vec{\mathrm{p}}^{\,2}/6m^2)\rangle\,, \tag{18}$$

where the matrix element is between two-component Schrödinger wave functions.

To Eq. (18) we must add a correction due to the $-i\vec{\gamma}_e\cdot\vec{\mathrm{E}}_e$ term. This term does not appear to be magnetic field dependent but its expectation value should be taken with wave functions which have been corrected due to the magnetic field dependence present in Eq. (5).[19] As discussed in Ref. 8, the primary effect is to modify the lower components of the wave function by replacing the factor $\vec{\sigma}_e\cdot\vec{\mathrm{p}}_e/2m$ by $\vec{\sigma}_e\cdot(\vec{\mathrm{p}}_e-e\vec{\mathrm{A}}_e)/2m$. This leads to a term

$$-(e/2m)(\alpha/2\pi)\langle(-e/m)\vec{\sigma}_e\cdot\vec{\mathrm{E}}_e\times\vec{\mathrm{A}}_e\rangle\,, \tag{19}$$

which for S states gives

$$-\frac{e}{2m}\,\frac{\alpha}{2\pi}\left\langle\frac{1}{3m}\,\frac{Z\alpha}{r}\,\vec{\sigma}_e\cdot\vec{\mathrm{H}}\,\frac{M}{m+M}\right\rangle\,. \tag{20}$$

Combining Eqs. (20) and (18), we obtain to order M^{-1}

$$\Delta E(M)=-\frac{e}{2m}\,\frac{\alpha}{2\pi}$$
$$\times\left\langle\vec{\sigma}_e\cdot\vec{\mathrm{H}}\left\{1-\frac{1}{3m}\left[\frac{\vec{\mathrm{p}}^{\,2}}{2m}+V\left(1-\frac{m}{M}\right)\right]\right\}\right\rangle\,, \tag{21}$$

which gives a ground-state result of

$$\Delta E(M)=-\frac{e}{2m}\,\frac{\alpha}{2\pi}\,\langle\vec{\sigma}_e\cdot\vec{\mathrm{H}}\rangle[1+\tfrac{1}{6}\,(Z\alpha)^2(1-2m/M)]\,. \tag{22}$$

The interaction of an electron with an external field must be corrected to account for vacuum polarization graphs on the photons exchanged between the electron and the source of the field. As discussed in Refs. 18 and 20, the energy shift due to vacuum polarization in a magnetic field is

$$\Delta E(\mathrm{VP})=\frac{\alpha}{2\pi}\left\langle\beta_e\vec{\mathrm{q}}^{\,2}\int_0^1 dv\,\frac{2v^2(1-\frac{1}{3}v^2)}{4m^2+\vec{\mathrm{q}}^{\,2}(1-v^2)}\,\vec{\gamma}\cdot\vec{\mathrm{A}}(\vec{\mathrm{q}})\right\rangle\,, \tag{23}$$

where here we are working in the momentum representation. For a constant magnetic field $\vec{\mathrm{A}}(\vec{\mathrm{q}})\sim\vec{\mathrm{H}}\times\vec{\nabla}_{\vec{\mathrm{q}}}\,\delta^3(\vec{\mathrm{q}})$ and therefore Eq. (23) should yield a zero result. This has already been discussed in Ref. 8 of Ref. 8(a). This null result disagrees with early work on this topic.[21]

Therefore it appears that in lowest-order the radiative level shifts are accounted for by introducing the Pauli interaction, in which the field is provided by the constant magnetic field and also by the Coulomb field.

V. UNITARY TRANSFORMATION OF HAMILTONIAN

The treatment given in the preceding sections depends critically on the correct determination of the wave function of the moving atom, as given by Eq. (4). The $\vec{\mathrm{K}}$ dependence in parentheses is crucial, even if the atom is at rest. The reason for this is that the operator $\vec{\mathrm{P}}$ does not commute with the full Hamiltonian, since the Hamiltonian depends on $\vec{\mathrm{X}}$ due to the interaction with the external field. Therefore simultaneous eigenstates of $\vec{\mathrm{P}}$ and of the full Hamiltonian do not exist, although simultaneous eigenstates of $\vec{\mathrm{P}}$ and the unperturbed Hamiltonian do exist. It is therefore desirable, if possible, to eliminate or to reduce the importance of $\vec{\mathrm{X}}$-dependent terms. This may be accomplished by means of a unitary transformation.

If the c.m. position operator $\vec{\mathrm{X}}$ was not a dynamical variable, we could make a gauge transformation which would eliminate the $\vec{\mathrm{X}}$ dependence from the Hamiltonian. Vector potentials $\frac{1}{2}\vec{\mathrm{H}}\times\vec{\mathrm{x}}_{e,p}$ would be altered to $\frac{1}{2}\vec{\mathrm{H}}\times(\vec{\mathrm{x}}_{e,p}-\vec{\mathrm{X}})$ by means of a gauge transformation and therefore, since $\vec{\mathrm{x}}_e-\vec{\mathrm{X}}$ and $\vec{\mathrm{x}}_p-\vec{\mathrm{X}}$ would not depend on $\vec{\mathrm{X}}$, neither would the Hamiltonian.

Of course, $\vec{\mathrm{X}}$ is an operator and it depends on both $\vec{\mathrm{x}}_e$ and $\vec{\mathrm{x}}_p$. Therefore it is not possible to gauge-transform $\vec{\mathrm{X}}$ away. However, by means of a unitary transformation it is possible to completely eliminate $\vec{\mathrm{X}}$ for a neutral system,[16] and also to reduce its importance in the case of a charged system.

Let

$$U=\exp(i\tfrac{1}{2}e\,\vec{\mathrm{x}}_e\cdot\vec{\mathrm{H}}\times\vec{\mathrm{X}})\exp(-i\tfrac{1}{2}Ze\,\vec{\mathrm{x}}_p\cdot\vec{\mathrm{H}}\times\vec{\mathrm{X}})$$
$$=\exp\left[i\,\frac{e}{2}\left(\frac{M+Zm}{m+M}\right)\vec{\mathrm{r}}\cdot\vec{\mathrm{H}}\times\vec{\mathrm{X}}\right] \tag{24}$$

be a unitary transformation such that $\psi=U\psi'$, where ψ is the complete eigenfunction of the original Hamiltonian.[22] Then ψ' will be an eigenfunction of $H'=U^{-1}HU$. Position operators are unaffected by U but momentum operators are transformed as

$$\begin{aligned}U^{-1}\vec{\mathrm{p}}_e\,U&=\vec{\mathrm{p}}_e+e[(M+Zm)/(m+M)]\,\vec{\mathrm{A}}(\vec{\mathrm{x}}_p)\,,\\ U^{-1}\vec{\mathrm{p}}_p\,U&=\vec{\mathrm{p}}_p-e[(M+Zm)/(m+M)]\,\vec{\mathrm{A}}(\vec{\mathrm{x}}_e)\,.\end{aligned} \tag{25}$$

As a consequence, the mechanical momenta are changed to

$$
\begin{aligned}
&U^{-1}[\vec{p}_e - e\vec{A}(\vec{x}_e)]\,U\\
&\quad = \vec{p}_e - e\vec{A}(\vec{r}) + [m(Z-1)/(m+M)]\,e\vec{A}(\vec{x}_p)\ ,\\
&U^{-1}[\vec{p}_p + Ze\vec{A}(\vec{x}_p)]\,U\\
&\quad = \vec{p}_p - Ze\vec{A}(\vec{r}) + [M(Z-1)/(m+M)]\,e\vec{A}(\vec{x}_e)\ ,
\end{aligned}
\tag{26}
$$

where $\vec{A}(\vec{x}) = \frac{1}{2}\vec{H}\times\vec{x}$. Equations (26) are independent of $\vec{X}$ for a neutral system but do depend on $\vec{X}$ if Z is different from unity.

Under the above transformation the new Hamiltonian (without Pauli interactions) H' becomes

$$
\begin{aligned}
H' = {}&\vec{\alpha}_e\cdot\left[\vec{p}_e - e\vec{A}(\vec{r}) + \frac{m(Z-1)}{m+M}\,e\vec{A}(\vec{x}_p)\right] + \beta_e m\\
&+\vec{\alpha}_p\cdot\left[\vec{p}_p - Ze\vec{A}(\vec{r}) + \frac{M(Z-1)}{m+M}\,e\vec{A}(\vec{x}_e)\right]\\
&+\beta_p M - Z\alpha/r + (Z\alpha/2r)\,[\vec{\alpha}_e\cdot\vec{\alpha}_p + \vec{\alpha}_e\cdot\hat{r}\,\vec{\alpha}_p\cdot\hat{r}]\ .
\end{aligned}
\tag{27}
$$

If $Z=1$, then $[H', \vec{P}]=0$ and therefore the exact eigenstates may be chosen as eigenstates of $\vec{P}$ as well as of H'. This was not the case previously. It should be pointed out that the unperturbed wave functions are identical to those previously given since the unperturbed problem is one for which the magnetic field is zero. However, in applying perturbation theory there are no longer any $\vec{X}$-dependent perturbations and therefore any $\vec{K}$-dependence in the unperturbed wave function will give rise to corrections which are "truly" motional. It follows now that if the atom is at rest, only the relative wave function is needed. Previously we found that the momentum dependence in the wave function gave nonvanishing corrections to the energy levels even in the zero momentum limit.

If $Z\neq 1$, then H' still contains $\vec{X}$ dependence and therefore $\vec{P}$ no longer commutes with H'. This implies that $\vec{X}$-dependent perturbations must again be treated with considerable caution, although in fact it turns out that these $\vec{X}$-dependent terms ultimately give a very small contribution.

The physical origin of the unitary transformation may be understood more completely by considering the operators $\tilde{\vec{\pi}}_e = \vec{p}_e + e\vec{A}(\vec{x}_e)$ and $\tilde{\vec{\pi}}_p = \vec{p}_p - Ze\vec{A}(\vec{x}_p)$. In the absence of any interaction between the electron and the nucleus these two operators are conserved since they both commute with the mechanical momenta $\vec{p}_e - e\vec{A}(\vec{x}_e)$ and $\vec{p}_p + Ze\vec{A}(\vec{x}_p)$. However, the components of these operators are noncommuting (e.g., $[\tilde{\pi}_{ex},\ \tilde{\pi}_{ey}]\neq 0$). This is a well-known result[23] and in the nonrelativistic problem $\tilde{\pi}_{ex,y}/m\omega$ gives the coordinate of the conserved center of the Landau orbit of the electron, where $\omega = -eH/m$. The same follows for the nucleus.

In the presence of interaction between the electron and the nucleus, $\tilde{\vec{\pi}}_e$ and $\tilde{\vec{\pi}}_p$ are no longer separately conserved but their sum $\tilde{\vec{\pi}} = \tilde{\vec{\pi}}_e + \tilde{\vec{\pi}}_p$ is conserved provided the interaction is a function only of the relative position. Moreover, for a neutral system $[\tilde{\pi}_x,\ \tilde{\pi}_y]=0$. As we turn on the interparticle the operator $\tilde{\vec{\pi}}$, which for the neutral noninteracting particle case is proportional to the conserved relative vector connecting the centers of the Landau orbits (NR case), continues to be conserved, although its physical meaning becomes obscure.

The previous statements may be summarized by the equations

$$
[\tilde{\pi}_i, H]=0,\quad [\tilde{\pi}_i, \tilde{\pi}_j] = -ie(1-Z)\epsilon_{ijk}H_k\ . \tag{28}
$$

The unitary transform of $\tilde{\pi}_i$ is $\tilde{P}_i$, i.e.,

$$
U^{-1}\,\tilde{\pi}_i\,U \equiv \tilde{P}_i = P_i - \tfrac{1}{2}e(Z-1)\,(\vec{H}\times\vec{X})_i\ , \tag{29}
$$

and therefore, since a unitary transformation preserves commutation relations, we have

$$
[\tilde{P}_i, H']=0,\quad [\tilde{P}_i, \tilde{P}_j] = -ie(1-Z)\epsilon_{ijk}H_k\ . \tag{30}
$$

Clearly, if the system is uncharged, $\tilde{P}_i$ is equal to P_i and therefore simultaneous eigenfunctions of P_i and H' exist. The unitary transformation takes the operator $\tilde{\pi}_i$ into P_i, the canonical momentum associated with the c.m. position. If the system is charged, eigenfunctions of $\tilde{P}_i$ and H' may be constructed but simultaneous eigenfunctions of $\tilde{P}_x$ and $\tilde{P}_y$ are not possible. Of course, if all magnetic interactions are treated perturbatively, the unperturbed eigenfunction will always be an eigenfunction of P_i and of the Hamiltonian in zero field. However, for a neutral system all perturbations commute with P_i when the H' form is used, whereas for a charged system there are some perturbations which do not commute with P_i. These must again be handled with great care.

It should be stressed that for a neutral system at rest the above analysis allows us to calculate the g factor with only knowledge of the relative wave function. However, if the system is charged or if we are specifically interested in motional effects, the $\vec{K}$ dependence of Eq. (4) is needed.

To further clarify the above unitary transformation and the motion of a composite system in a constant magnetic field we discuss the classical Lorentz force law for two interacting particles having charges of e_1 and e_2. We have

$$
m_1\ddot{\vec{x}}_1 = e_1\dot{\vec{x}}_1\times\vec{H} + \vec{F}_{12},\quad m_2\ddot{\vec{x}}_2 = e_2\dot{\vec{x}}_2\times\vec{H} + \vec{F}_{21}\ . \tag{31}
$$

Adding these two equations and using Newton's third law, we obtain

$$
\frac{d}{dt}\,[m_1\dot{\vec{x}}_1 + e_1\vec{H}\times\vec{x}_1 + m_2\dot{\vec{x}}_2 + e_2\vec{H}\times\vec{x}_1] = 0\ . \tag{32}
$$

But since $m_1\dot{\vec{x}}_1 = \vec{p}_1 - e_1\vec{A}(\vec{x}_1)$ and $m_2\dot{\vec{x}}_2 = \vec{p}_2 - e_2\vec{A}(\vec{x}_2)$, we obtain

$$
\frac{d}{dt}\,[\vec{p}_1 + e_1\vec{A}(\vec{x}_1) + \vec{p}_2 + e_2\vec{A}(\vec{x}_2)] = 0\ . \tag{33}
$$

Thus the conserved quantity $\vec{\vec{\pi}}$ discussed earlier emerges from purely classical considerations.

Now let $\vec{K}$ be the constant value of $\vec{\vec{\pi}}$. We then obtain the differential equation

$$(m_1+m_2)\dot{\vec{X}}+(e_1+e_2)\vec{H}\times\dot{\vec{X}}+\frac{e_1m_2-e_2m_1}{m_1+m_2}\vec{H}\times\dot{\vec{r}}=\vec{K}\ . \tag{34}$$

For a neutral system this equation is easily solved for $\vec{X}$ to obtain

$$\vec{X}(t)=\frac{\vec{K}}{m_1+m_2}t-e_1\vec{H}\times\int_0^t\vec{r}(t')dt'\ . \tag{35}$$

If we neglect the second term of Eq. (35), the center of mass would move in a straight line. If the internal forces $\vec{F}_{12}$ cause $\vec{r}$ to describe a *small* periodic orbit (which is the case for a "classical" H atom), then the motion of the center of mass presumably fluctuates slightly about straight-line motion owing to the time dependence of $\vec{r}(t)$.

For a charged system, Eq. (34) may readily be solved if we ignore the $\dot{\vec{r}}$-dependent term. The center of mass will describe a circular or helical orbit. This is presumably perturbed because of the presence of $\dot{\vec{r}}$, and we therefore expect fluctuations about the gross motion.

As discussed in Sec. IV, the radiative corrections are accounted for by introducing a Pauli interaction. This takes care of the electron's anomalous moment. The nucleus also has an anomalous moment which is due to the meson cloud. Therefore a Pauli interaction, introduced phenomenologically, is also needed for the nucleus. Since these interactions are not momentum dependent, they are unaffected by the unitary transformation. Therefore the addition to H' of Eq. (27) is H_{IM} (IM denotes intrinsic moment or Pauli moment), where[24]

$$H_{\mathrm{IM}}=-\frac{Z\alpha}{2m}a_e\left(i\beta_e\vec{\alpha}_e\cdot\frac{\vec{r}}{r^3}-\beta_e\vec{\sigma}_e\cdot\vec{\alpha}_p\times\frac{\vec{r}}{r^3}\right)-\frac{e}{2m}a_e\beta_e\vec{\sigma}_e\cdot\vec{H}+\frac{Z\alpha}{2M}a_p\left(i\beta_p\vec{\alpha}_p\cdot\frac{\vec{r}}{r^3}-\beta_p\vec{\sigma}_p\cdot\vec{\alpha}_e\times\frac{\vec{r}}{r^3}\right)+\frac{Ze}{2M}a_p\beta_p\vec{\sigma}_p\cdot\vec{H}$$

$$+\beta_e\beta_p\frac{Z\alpha}{4mM}a_ea_p\left(\frac{\vec{\sigma}_e\cdot\vec{\sigma}_p}{r^3}-\frac{3\vec{\sigma}_e\cdot\hat{r}\vec{\sigma}_p\cdot\hat{r}}{r^3}-\frac{8\pi}{3}\vec{\sigma}_e\cdot\vec{\sigma}_p\delta^3(\vec{r})\right)\ . \tag{36}$$

Here a_e and a_p denote the anomalous moments in units of the Bohr magneton and the nuclear magneton, respectively.

Using the total transformed Hamiltonian $H'+H_{\mathrm{IM}}$ we may repeat our earlier calculation of the electron g factor. The results are unchanged. As mentioned earlier, our unperturbed wave functions are approximate and would have to be corrected in order to obtain g-factor corrections of relative order $(Z\alpha)^2m^2/M^2$. Since we are interested in terms of this order, we prefer to use the alternative procedure of making a Foldy-Wouthuysen[25]-type transformation. These transformations have been discussed by Chraplyvy[26] and by Barker and Glover.[24] We apply this method in Sec. VI.

VI. CHRAPLYVY-BARKER-GLOVER REDUCTION OF HAMILTONIAN

We now perform a reduction of the Hamiltonian $H'+H_{\mathrm{IM}}$ by means of the Chraplyvy-Barker-Glover method. This is essentially a Foldy-Wouthuysen-type transformation for two particles, and affords an expansion of the Hamiltonian in inverse powers of the electron and proton masses. An expansion of the Hamiltonian to orders $1/m^3$, $1/M^3$, and $1/mM$ allows calculation of the g factors to relative orders $(Z\alpha)^2m^2/M^2$ and $\alpha(Z\alpha)^2m^2/M^2$. This method also provides a simple physical interpretation for the bound-state corrections to the g factors, as noted in Ref. 9.

Chraplyvy, Barker, and Glover found a unitary transformation which transforms a two-body Hamiltonian of the form

$$H=\beta^{\mathrm{I}}m_{\mathrm{I}}+\beta^{\mathrm{II}}m_{\mathrm{II}}+(\mathcal{E}\mathcal{E})+(\mathcal{O}\mathcal{E})+(\mathcal{E}\mathcal{O})+(\mathcal{O}\mathcal{O}) \tag{37}$$

into an even-even operator

$$H_{\mathrm{TR}}=\beta^{\mathrm{I}}m_{\mathrm{I}}+\beta^{\mathrm{II}}m_{\mathrm{II}}+(\mathcal{E}\mathcal{E})+\frac{\beta^{\mathrm{I}}}{2m_{\mathrm{I}}}(\mathcal{O}\mathcal{E})^2+\frac{\beta^{\mathrm{II}}}{2m_{\mathrm{II}}}(\mathcal{E}\mathcal{O})^2-\frac{\beta^{\mathrm{I}}}{8m_{\mathrm{I}}^3}(\mathcal{O}\mathcal{E})^4-\frac{\beta^{\mathrm{II}}}{8m_{\mathrm{II}}^3}(\mathcal{E}\mathcal{O})^4+\frac{1}{8m_{\mathrm{I}}^2}[[(\mathcal{O}\mathcal{E}),(\mathcal{E}\mathcal{E})],(\mathcal{O}\mathcal{E})]$$

$$+\frac{1}{8m_{\mathrm{II}}^2}[[(\mathcal{E}\mathcal{O}),(\mathcal{E}\mathcal{E})],(\mathcal{E}\mathcal{O})]+\frac{\beta^{\mathrm{I}}\beta^{\mathrm{II}}}{4m_{\mathrm{I}}m_{\mathrm{II}}}[[(\mathcal{O}\mathcal{E}),(\mathcal{O}\mathcal{O})]_+,(\mathcal{E}\mathcal{O})]_++\cdots\ . \tag{38}$$

The above notation is that of Barker and Glover. The symbols $(\mathcal{E}\mathcal{E})$, $(\mathcal{O}\mathcal{E})$, $(\mathcal{E}\mathcal{O})$, and $(\mathcal{O}\mathcal{O})$ refer to operators which are even-even, odd-even, even-odd, and odd-odd with respect to the Dirac matrices for the two particles. In our case we have

$$(\mathcal{E}\mathcal{E})=-\frac{Z\alpha}{r}-\frac{e}{2m}a_e\beta_e\vec{\sigma}_e\cdot\vec{H}+\frac{Ze}{2M}a_p\beta_p\vec{\sigma}_p\cdot\vec{H}$$

$$+\frac{Z\alpha}{4mM}\,\beta_e\beta_p a_e a_p\left[\frac{8\pi}{3}\,\vec{\sigma}_e\cdot\vec{\sigma}_p\,\delta^3(\vec{r})\right.$$

$$\left.+\frac{3\vec{\sigma}_e\cdot\hat{r}\,\vec{\sigma}_p\cdot\hat{r}-\vec{\sigma}_e\cdot\vec{\sigma}_p}{r^3}\right],$$

$$(\mathcal{O}\mathcal{E})=\vec{\alpha}_e\cdot\left[\vec{p}_e-e\vec{A}(\vec{r})+\frac{m}{m+M}\,(Z-1)\,e\vec{A}(\vec{x}_p)\right]$$

$$-\frac{iZ\alpha}{2m}\,a_e\beta_e\,\frac{\vec{\alpha}_e\cdot\vec{r}}{r^3}-\frac{Z\alpha}{2M}\,\beta_p a_p\vec{\sigma}_p\cdot\frac{\vec{\alpha}_e\times\vec{r}}{r^3}\quad,$$

$$(\mathcal{E}\mathcal{O})=\vec{\alpha}_p\cdot\left[\vec{p}_p-Ze\vec{A}(\vec{r})+\frac{M}{m+M}\,(Z-1)\,e\vec{A}(\vec{x}_e)\right]$$

$$+\frac{iZ\alpha}{2M}\,a_p\beta_p\,\frac{\vec{\alpha}_p\cdot\vec{r}}{r^3}+\frac{Z\alpha}{2m}\,a_e\beta_e\vec{\sigma}_e\cdot\frac{\vec{\alpha}_p\times\vec{r}}{r^3}\quad,$$

$$(\mathcal{O}\mathcal{O})=(Z\alpha/2r)\,(\vec{\alpha}_e\cdot\vec{\alpha}_p+\vec{\alpha}_e\cdot\hat{r}\,\vec{\alpha}_p\cdot\hat{r})\;, \tag{39}$$

and the transformed Hamiltonian becomes (setting $\beta_e=1$, $\beta_p=1$ for positive-energy states)

$$H_{\mathrm{TR}}=M+m+\sum_{n=0}^{7}H_n\;,$$

$$H_0=\frac{\vec{\pi}_e^{\,2}}{2m}+\frac{\vec{\pi}_p^{\,2}}{2M}-\frac{Z\alpha}{r}\;,\quad H_1=-\frac{\vec{\pi}_e^{\,4}}{8m^3}-\frac{\vec{\pi}_p^{\,4}}{8M^3}\;,$$

$$H_2=\frac{\pi Z\alpha}{2m^2}(1+2a_e)\,\delta^3(\vec{r})+\frac{\pi Z\alpha}{2M^2}\,(1+2a_p)\,\delta^3(\vec{r})\;,$$

$$H_3=\frac{Z\alpha}{4m^2}\,(1+2a_e)\,\vec{\sigma}_e\cdot\frac{\vec{r}\times\vec{\pi}_e}{r^3}-\frac{Z\alpha}{4M^2}\,(1+2a_p)\,\vec{\sigma}_p\cdot\frac{\vec{r}\times\vec{\pi}_p}{r^3}\quad, \tag{40}$$

$$H_4=-\frac{Z\alpha}{2mM}\,(1+a_e)\,\vec{\sigma}_e\cdot\frac{\vec{r}\times\vec{\pi}_p}{r^3}+\frac{Z\alpha}{2mM}\,(1+a_p)\,\vec{\sigma}_p\cdot\frac{\vec{r}\times\vec{\pi}_e}{r^3}\quad,$$

$$H_5=-\frac{e}{2m}\left[\vec{\sigma}_e\cdot\vec{H}\left(1-\frac{\vec{\pi}_e^{\,2}}{2m^2}\right)+a_e\left(\vec{\sigma}_e\cdot\vec{H}-\frac{\vec{\sigma}_e\cdot\vec{\pi}_e\,\vec{\pi}_e\cdot\vec{H}}{2m^2}\right)\right]$$

$$+\frac{Ze}{2M}\left[\vec{\sigma}_p\cdot\vec{H}\left(1-\frac{\vec{\pi}_p^{\,2}}{2M^2}\right)\right.$$

$$\left.+a_p\left(\vec{\sigma}_p\cdot\vec{H}-\frac{\vec{\sigma}_p\cdot\vec{\pi}_p\,\vec{\pi}_p\cdot\vec{H}}{2M^2}\right)\right]\;,$$

$$H_6=\frac{Z\alpha}{2mM}\left[\frac{1}{r}\,\vec{\pi}_e\cdot\vec{\pi}_p+\vec{r}\left(\frac{\vec{r}}{r^3}\cdot\vec{\pi}_e\right)\cdot\vec{\pi}_p\right]\quad,$$

$$H_7=\frac{Z\alpha}{4mM}\,(1+a_e)\,(1+a_p)\left[\frac{8\pi}{3}\,\vec{\sigma}_e\cdot\vec{\sigma}_p\,\delta^3(\vec{r})\right.$$

$$\left.+\frac{3\vec{\sigma}_e\cdot\vec{r}\,\vec{\sigma}_p\cdot\vec{r}-\vec{\sigma}_e\cdot\vec{\sigma}_p r^2}{r^5}\right]\;,$$

where we have defined

$$\vec{\pi}_e\equiv\vec{p}_e-e\vec{A}(\vec{r})+[m/(M+m)]\,(Z-1)\,e\vec{A}(\vec{x}_p)$$

$$=\vec{p}+\frac{m}{M+m}\,\vec{P}-\left[1+(Z-1)\left(\frac{m}{M+m}\right)^2\right]e\vec{A}(\vec{r})$$

$$+(Z-1)\frac{m}{M+m}\,e\vec{A}(\vec{X})\quad, \tag{41}$$

$$\vec{\pi}_p\equiv\vec{p}_p-Ze\vec{A}(\vec{r})+[M/(M+m)]\,(Z-1)\,e\vec{A}(\vec{x}_e)$$

$$=-\vec{p}+\frac{M}{M+m}\,\vec{P}-\left[Z-(Z-1)\left(\frac{M}{M+m}\right)^2\right]$$

$$\times e\vec{A}(\vec{r})+(Z-1)\frac{M}{M+m}\,e\vec{A}(\vec{X})\quad.$$

Many of the terms appearing in our transformed Hamiltonian have already been obtained by Barker and Glover. However, with an external magnetic field present, there are additional field-dependent terms which contribute to the energy of the atom. From these terms the g factors of the particles may be calculated.

In order to calculate the g factors we first expand the terms in Eq. (40) containing $\vec{\pi}_e$ and $\vec{\pi}_p$, making use of Eq. (41). This expansion results in numerous terms containing both relative and c.m. variables. For example, H_0 becomes

$$H_0=\frac{\vec{P}^2}{2(M+m)}+\frac{\vec{p}^{\,2}}{2m_{\mathrm{reduced}}}-\frac{Z\alpha}{r}-\frac{M+Zm}{(M+m)^2}\,e\vec{P}\times\vec{H}\cdot\vec{r}-\frac{e}{2m}\left[1-Z\frac{m}{M}-(1-Z)\frac{m}{M+m}\right]\vec{r}\times\vec{p}\cdot\vec{H}-\frac{e(1-Z)}{2(M+m)}\,\vec{X}\times\vec{P}\cdot\vec{H}$$

$$+\frac{e^2}{2m}\left[1+Z^2\frac{m}{M}+(1-Z)^2\,\frac{m(m^3+M^3)}{(M+m)^4}-2(1-Z)\,\frac{m(m-ZM)}{(M+m)^2}\right]\vec{A}(\vec{r})^2$$

$$+\frac{e^2}{2(M+m)}\,(1-Z)^2\vec{A}(\vec{X})^2+2e^2\,(1-Z)\,\frac{M+Zm}{(M+m)^2}\,\vec{A}(\vec{r})\cdot\vec{A}(\vec{X})\quad. \tag{42}$$

The other terms, H_1, H_2, ..., in Eq. (40) may also be expressed in relative and c.m. variables after some straightforward calculations. Neglecting motional terms such as $\vec{X}\times\vec{P}\cdot\vec{H}$ and quadratic field-dependent terms such as $\vec{A}^2$, which are discussed in Sec. VII, we use first-order perturbation theory with the nonrelativistic Pauli-Schrödinger $1S$ eigenfunction to evaluate H'_{mag} between the spatial part of the wave function. We obtain

$$\langle H'_{\mathrm{mag}}\rangle=-\frac{e}{2m}\;\tfrac{1}{2}g_e\langle\vec{\sigma}_e\cdot\vec{H}\rangle\left\{1-\tfrac{1}{2}(Z\alpha)^2\left(\frac{M}{M+m}\right)^2\frac{1+\frac{1}{3}a_e}{1+a_e}+\tfrac{1}{6}\,(Z\alpha)^2\,\frac{M}{M+m}\,\frac{1+2a_e}{1+a_e}\left[1+(Z-1)\left(\frac{m}{M+m}\right)^2\right]\right.$$

$$-\tfrac{1}{3}(Z\alpha)^2\frac{m}{M+m}\left[Z-(Z-1)\left(\frac{M}{M+m}\right)^2\right]\Bigg\}+\frac{Ze}{2M}\,\tfrac{1}{2}g_p\langle\vec{\sigma}_p\cdot\vec{\mathrm{H}}\rangle\Bigg\{1-\tfrac{1}{2}(Z\alpha)^2\left(\frac{m}{M+m}\right)^2\frac{1+\frac{1}{3}a_p}{1+a_p}$$

$$+\tfrac{1}{6}Z\alpha^2\frac{m}{M+m}\,\frac{1+2a_p}{1+a_p}\left[Z-(Z-1)\left(\frac{M}{M+m}\right)^2\right]-\tfrac{1}{3}Z\alpha^2\frac{M}{M+m}\left[1+(Z-1)\left(\frac{m}{M+m}\right)^2\right]\Bigg\},\qquad(43)$$

where H'_{mag} is the magnetic-field-dependent part of the transformed Hamiltonian.

It should be stressed that for a charged system H'_{mag} still does not commute with $\vec{\mathrm{P}}$ and therefore in doing perturbation theory we should really retain the momentum-dependence of the wave function (as in Sec. III); i.e., the wave function really does not assume a Pauli-Schrödinger form since the effect of terms in H_3 and H_4 must be included in the wave function [see also Ref. 8(b)]. However, it turns out that those terms in H'_{mag} which do not commute with $\vec{\mathrm{P}}$ are extremely small and do not, therefore, necessitate inclusion of momentum dependence in the wave function, except, of course, if we are specifically examining motional corrections.

Contributions to Eq. (43) arise from the perturbation terms H_3, H_4, and H_5 of Eq. (40). Expanding to order m^2/M^2 in the masses and setting $a_e=\alpha/2\pi$, we find for the g factors

$$g_e(1S)=g_e\Bigg\{1-\tfrac{1}{3}(Z\alpha)^2\left[1-\frac{3}{2}\frac{m}{M}+\frac{3}{2}(1+Z)\frac{m^2}{M^2}\right]+\frac{1}{4\pi}\alpha(Z\alpha)^2\left[1-\frac{5}{3}\frac{m}{M}+\frac{6+Z}{3}\frac{m^2}{M^2}\right]\Bigg\},$$

$$g_p(1S)=g_p\left[1-\tfrac{1}{3}Z\alpha^2+\tfrac{1}{6}Z\alpha^2\frac{m}{M}\,\frac{3+4a_p}{1+a_p}-\tfrac{1}{6}Z\alpha^2\frac{m^2}{M^2}\,\frac{3(Z+1)+(6-Z)a_p}{1+a_p}\right].\qquad(44)$$

VII. SUMMARY

Our final results for the electron and nuclear g factors for the hydrogenic $1S$ state are expressed in Eq. (44). We expect that these results are correct to relative orders $(Z\alpha)^2m^2/M^2$ and $\alpha(Z\alpha)^2m^2/M^2$. Additional corrections should be of relative orders $(Z\alpha)^4$ and $(Z\alpha)^4m/M$. Equation (44) is the result reported by both of us previously.[8,9] It has been independently confirmed by the recent work of Faustov[27] and also by Close and Osborn.[28]

The present authors and those of Refs. 27 and 28 have employed somewhat different approaches to the calculation of magnetic moments, although each method employs a single-time formalism. Our approach has been to start with the Breit Hamiltonian and to give a quantum-mechanical treatment in the Dirac representation (Sec. III) and also the Foldy-Wouthuysen representation (Sec. VI). We have also demonstrated the usefulness of using unitary transformations (Sec. V) to simplify the quantum-mechanical treatment. The work of Faustov is based on the quasipotential method, in which a single-time formalism is obtained using the two-time Green's function of the composite system. Matrix elements of the electromagnetic current operator are obtained between states of different total momenta, and the magnetic moment is extracted by evaluating the derivative of this matrix element at zero-momentum transfer. The work of Close and Osborn is based on approximate realizations of the Poincaré group in the Foldy-Wouthuysen representation. The generators for the composite system are constructed from the individual particle dynamical variables, which are then expressed in terms of c.m. and internal dynamical variables (which differ from the variables $\vec{\mathrm{X}}$ and $\vec{\mathrm{r}}$ used in this paper). In terms of these variables the Hamiltonian is separable. The total electromagnetic current (obtained partly through reduction of the Dirac equation) is also expressed in terms of these variables and the magnetic moment is readily evaluated.

From an experimentalist's point of view there may be motional corrections to the g factors. These would be of relative order $\vec{\mathrm{V}}^2/c^2$, where $\vec{\mathrm{V}}$ is the atomic velocity, and could be important when very high precision is required. There are also possible corrections to the g factors if the magnetic field is not small. We find, however, that these are extremely small for the ground state [of relative order $\alpha^2(eH/m\,\mathrm{Ry})^2$] and are of order $\alpha^2(eH/m\,\mathrm{Ry})$ for states with nonzero orbital angular momentum.

The energy levels are also shifted due to diamagnetic corrections but these do not affect the g factors. They shift the various hyperfine levels of a particular electronic state by the same amount. For an ion the $(\vec{\mathrm{X}}\times\vec{\mathrm{P}})\cdot\vec{\mathrm{H}}$ term of Eq. (42) gives the interaction of the translational orbital motion with the magnetic field and this also has no effect on the g factors.

These results may be applied to existing experiments[1] involving hydrogen and deuterium, as both of us have noted previously.[8,9] From Eq. (44) we calculate a numerical value for the bound-state correction to the electron-proton g-factor ratio for atomic hydrogen $g_e(1S,\mathrm{H})/g_p(1S,\mathrm{H})=(g_e/g_p)(1+2.8\times10^{-8})$. This value may be applied as a theoretical correction to the measured value of $g_e(1S,\mathrm{H})/g_p(1S,\mathrm{H})$ (see Kleppner[1]) to obtain a precise value for the magnetic moment of the proton in units of the Bohr magneton. We also calculate from Eq. (44) a numerical value for the hydrogen-deuterium g-factor ratio $R=g_e(1S,\mathrm{H})/g_e(1S,\mathrm{D})=1+7.22\times10^{-9}$. This calculation is in excellent agreement with the measurement of Hughes and Robinson,[1] $R=1+(7.2\pm1.2)\times10^{-9}$, and in slight disagreement with the measurement of Larson, Valberg, and Ramsey,[1] $R=1+(9.4\pm1.4)\times10^{-9}$. Measurements of R of even greater precision are in progress which will hopefully test our $(Z\alpha)^2m^2/M^2$ and $\alpha(Z\alpha)^2m/M$ corrections, each of which contributes about -0.01×10^{-9} to R, as well as the dominant $(Z\alpha)^2m/M$ contribution.

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APPENDIX: CENTER-OF-MASS DEPENDENCE OF WAVE FUNCTION

We would like to show here that $\psi_K(\vec{r},\vec{X})$ given in Eq. (4) is an eigenfunction of the Hamiltonian of Eq. (3). We know that $H_{\mathrm{rel}}\,\psi_0(\vec{r})=\mathfrak{M}\psi_0(\vec{r})$ and we wish to correct the wave function due to the term H_P in the Hamiltonian.

We assume a solution of the form

$$\psi_K(\vec{r},\vec{X})=\left(1+\frac{\vec{\alpha}_e\cdot\vec{K}}{2\mathfrak{M}}+\frac{i\eta(r)}{\mathfrak{M}}\,\vec{K}\cdot\vec{r}\right)\psi_0(\vec{r})e^{i\vec{K}\cdot\vec{x}},\tag{A1}$$

where $\eta(r)$ is a function of the relative coordinate to be determined (if possible) in such a way that (A1) is an eigenfunction of Eq. (3). Now $H\psi_K(\vec{r},\vec{X})$ is equal to

$$H_{\mathrm{rel}}\,\psi_0(\vec{r})e^{i\vec{K}\cdot\vec{x}}+H_{\mathrm{rel}}\left(\frac{\vec{\alpha}_e\cdot\vec{K}}{2\mathfrak{M}}+\frac{i\eta}{\mathfrak{M}}\,\vec{K}\cdot\vec{r}\right)\psi_0(\vec{r})e^{i\vec{K}\cdot\vec{x}}$$
$$+H_P\psi_0(\vec{r})e^{i\vec{K}\cdot\vec{x}}+H_P\left(\frac{\vec{\alpha}_e\cdot\vec{K}}{2\mathfrak{M}}+\frac{i\eta}{\mathfrak{M}}\,\vec{K}\cdot\vec{r}\right)\psi_0(\vec{r})e^{i\vec{K}\cdot\vec{x}}\;.\tag{A2}$$

In this expression we will ignore terms such as $(K/M^2)pV$, $(K^2/M^2)V$, etc., i.e., terms of order KM^{-2} which bring in binding corrections. We then obtain

$$\Bigg[\mathfrak{M}+(\vec{\alpha}_e\cdot\vec{p}+\beta_e m+V+M)\left(\frac{\vec{\alpha}_e\cdot\vec{K}}{2\mathfrak{M}}+\frac{i\eta}{\mathfrak{M}}\,\vec{K}\cdot\vec{r}\right)$$
$$+\frac{m}{m+M}\,\vec{\alpha}_e\cdot\vec{K}-\frac{\vec{p}\cdot\vec{K}}{m+M}+\frac{\vec{K}^2}{2(m+M)}-\frac{V}{2(m+M)}$$
$$\times(\vec{\alpha}_e\cdot\vec{K}+\vec{\alpha}_e\cdot\hat{r}\;\hat{r}\cdot\vec{K})\Bigg]\psi_0(\vec{r})e^{i\vec{K}\cdot\vec{x}}\;.\tag{A3}$$

After considerable rearrangements are made we obtain

$$\Bigg[\mathfrak{M}\left(1+\frac{\vec{\alpha}_e\cdot\vec{K}}{2\mathfrak{M}}+\frac{i\eta}{\mathfrak{M}}\,\vec{K}\cdot\vec{r}\right)+\frac{\vec{K}^2}{2(m+M)}+\left(\frac{V}{2}-\epsilon\right)\frac{\vec{\alpha}_e\cdot\vec{K}}{m+M}$$
$$+\frac{i}{\mathfrak{M}}\,\vec{\alpha}_e\cdot[\vec{p},\eta\vec{K}\cdot\vec{r}\,]-\frac{V}{2(m+M)}\,\vec{\alpha}_e\cdot\hat{r}\;\hat{r}\cdot\vec{K}\Bigg]\psi_0(\vec{r})e^{i\vec{K}\cdot\vec{x}}\;,\tag{A4}$$

where $\epsilon=\mathfrak{M}-m-M$. Ignoring all K^3 terms, we have

$$\simeq\left(\mathfrak{M}+\frac{\vec{K}^2}{2(m+M)}\right)\left(1+\frac{\vec{\alpha}_e\cdot\vec{K}}{2\mathfrak{M}}+\frac{i\eta}{\mathfrak{M}}\,\vec{K}\cdot\vec{r}\right)\psi_0(\vec{r})e^{i\vec{K}\cdot\vec{x}}$$
$$+\Bigg[\left(\frac{V}{2}-\epsilon\right)\frac{\vec{\alpha}_e\cdot\vec{K}}{m+M}+\frac{i}{\mathfrak{M}}\,\vec{\alpha}_e\cdot\,[\vec{p},\eta\vec{K}\cdot\vec{r}\,]$$
$$-\frac{V}{2(m+M)}\,\vec{\alpha}_e\cdot\hat{r}\;\hat{r}\cdot\vec{K}\Bigg]\psi_0(\vec{r})e^{i\vec{K}\cdot\vec{x}}\;.\tag{A5}$$

The choice $\eta=\epsilon-\frac{1}{2}V$ causes the second line of (A5) to vanish (within our approximation), and therefore (A1) is in fact an eigenfunction of H with eigenvalue $m+M+\epsilon+\vec{K}^2/2(m+M)$. Note that, owing to the approximations made, the kinetic-energy term could just as well be $\vec{K}^2/2\mathfrak{M}$ and the η-dependent term in (A1) could be $[i\eta/(m+M)]\vec{K}\cdot\vec{r}$.

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equation is correct except for terms of order $\langle e\not{A}\,\tilde{g}/mM\rangle$, where $\tilde{g}$ is the BS kernel (or potential). Since the calculations presented in this paper are only to first order in binding, we conclude that minimal coupling of the Breit equation is valid to the accuracy required.

[15] See Eqs. (8) and (9), which are valid expressions even between different eigenstates of $\vec{P}$. In this section we are assuming a scalar nucleus. In the more general case we also write $\langle H_{\text{mag}}\rangle$, but if there is nuclear spin, this expectation value does not give the energy shift. Degenerate perturbation theory is needed because of the various total spin states which are possible; this leads to the Breit-Rabi formula. In evaluating expressions like $\langle H_{\text{mag}}\rangle$ we are merely evaluating the spatial parts, which for the 1S state are the same regardless of the spin-dependent part of the wave function.

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Theory of One-Electron Molecules. I. Li_2^+

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An accurate method for solving the one-electron Schrödinger equation for small molecules is presented. For Li_2^+, the valence-electron-core interaction is treated as an effective potential found by fitting the atomic energy levels. The intermolecular potentials for six low-lying electronic states of Li_2^+ are calculated. For the ground state σ_{g1}, a binding energy of 1.30 eV is found at a separation of 3.08 Å and a vibration frequency of 277 cm^{-1}. From the intermolecular potentials, three cross sections are calculated for Li ions scattering from Li atoms: (i) elastic scattering, (ii) charge transfer, and (iii) inelastic scattering leaving the atom in a 2p excited state. This last process proceeds through a curve crossing of the σ_{u1} and π_{u1} states at $R = 5.95a_0$.

I. INTRODUCTION

An accurate and convenient numerical method for solving the one-electron Schrödinger equation for small molecules is presented. This method is applied to the calculation of the intermolecular potentials of six low-lying electronic states of the Li_2^+ molecule. The interaction between the valence electron and the core electrons is treated as an effective potential which is determined by fitting the atomic energy levels of the Li atom. As long as the cores of the Li^+ ions do not overlap appreciably, this effective potential should provide an accurate physical model for Li_2^+. For the ground state σ_{g1}, a binding energy of 1.30 eV is found at an internuclear separation of $R = 5.85a_0$ and a vibration frequency of 277 cm^{-1}.

From the intermolecular potentials we can calculate the cross sections for the three scattering processes that have been studied experimentally: (i) the elastic differential scattering cross section for lithium ions bombarding lithium atoms[1] $Li^+ + Li \rightarrow Li^+ + Li$, (ii) the total charge-transfer cross section[2,3] $Li^+ + Li \rightarrow Li + Li^+$, and (iii) the inelastic differential cross section for the process in which the lithium atom is excited from the 2s ground state to the 2p state.[1] This last process goes at low energy via a curve crossing of the σ_{u1} and π_{u1} states at $R = 5.95a_0$. We calculate the transition probability $\sigma_{u1} \rightarrow \pi_{u1}$ as a function of ion velocity and impact parameter by integrating the time-dependent Schrödinger equation numerically for