

Theory of Hyperfine Stark Shifts in Many-Electron Systems: Application to Lithium*

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(Received 27 November 1972)

The linked-cluster many-body perturbation theory has been applied to the study of the quadratic Stark shift of the hyperfine transition frequency of lithium atom. This procedure provides a method of quantitatively analyzing the relative importance of one- and many-electron contributions to the hyperfine Stark shift. The theoretical result $\delta\nu = -(5.2 \pm 0.3) \times 10^{-8} \epsilon^2 \text{ Hz}/(\text{V/cm})^2$ obtained for lithium is in substantial agreement (86%) with the recently measured value $\delta\nu = -(6.1 \pm 0.2) \times 10^{-8} \epsilon^2$ approaching the situation in the hydrogen atom.

Recent measurements¹ on the influence of electric fields on the hyperfine transition frequencies in the alkali-metal atoms pose a challenge to our theoretical understanding of electronic structure of atoms since it simultaneously requires accurate knowledge of the electronic wave function near the nucleus for the hyperfine interaction and the peripheral region for the electric-field perturbation. This article is aimed at demonstrating for the first time that a first-principles many-body calculation of this hyperfine Stark shift (HSS) effect can give a clear understanding of the mechanisms that contribute to this effect and can provide agreement with experiment to the same order as currently exists^{2,3} for the ideal case, the hydrogen atom. Although specific quantitative application is made here to the case of lithium atom and comparison is made with experiment, the procedure adopted is directly applicable without modification to more complicated systems, such as the heavier alkali-metal atoms as well as the fifth-group atoms, the latter being potentially more interesting from a many-body point of view.⁴

A theoretical analysis of the HSS in many-electron atoms and molecules essentially requires the perturbation of the exact wave function for the atom by two orders in the applied electric field and one order in the hyperfine interaction. Since exact many-electron wave functions are not usually available, it is convenient to utilize a set of states derived from a single-particle potential as a basis for the perturbation treatment of the problem. However, for both hyperfine effects^{4,5} in isolated atoms and electric-field shielding effects,⁶ it is well-known⁷ that many-body correlation effects are often important. One therefore needs a procedure which can include correlation effects in both the presence and absence of the electric field in a straightforward way, such as the linked-cluster many-body perturbation-theory (LCMBPT) approach⁴ adopted here.

In this approach, one handles all three perturba-

tion terms, the electric field term H_ϵ , the hyperfine Hamiltonian H_{hfs} , and the electron-electron interaction through the diagrammatic perturbation procedure (the last being included in principle) to all orders. In keeping with the convention usually adopted,¹ the quadratic HSS $\delta\nu$ is defined by the relation

$$\delta\nu = \nu(\vec{\epsilon}) - \nu(0) = \kappa\epsilon^2, \quad (1)$$

$\nu(\epsilon)$ and $\nu(0)$ being the hyperfine transition frequencies between the $F = J + I$ and $F = J + I - 1$ levels, in the presence and absence of the electric field $\vec{\epsilon}$, respectively. The constant κ in Eq. (1) is measured by experiment¹ and is the quantity to be calculated here. Considering only the magnetic hyperfine Hamiltonian in a $|FM_J J\rangle$ representation and utilizing the techniques of Racah algebra, one obtains

$$\nu = \frac{I+J}{hJ} \sum_{k=0}^2 \langle JM_J = J | T_0^{(k)} | JM_J = J \rangle. \quad (2)$$

Here we have taken $H_{\text{hfs}} = I^{(1)} \cdot [T^{(1)}(0) + T^{(1)}(1) + T^{(1)}(2)]$ as the tensor-product form of the Hamiltonian with the labels $k = 0, 1, 2$ in Eq. (2) denoting, respectively, the Fermi-contact, magnetic-orbital, and spin-dipolar operators. For the nuclear-quadrupole contribution to the HSS, one obtains a similar expression for the general case $J > \frac{1}{2}$.

In Eq. (2) the $|JM_J = J\rangle$ represent the electronic wave functions for the system in the absence and presence of the electric field $\vec{\epsilon}$, where in the latter case J (and M_J) characterize the corresponding state in the absence of $\vec{\epsilon}$. In the LCMBPT procedure these wave functions are given by the linked-cluster expansion,^{5,8} namely,

$$\Psi = \sum_n \left(\frac{1}{E_0 - H_0} H'' \right)^n \Phi_0. \quad (3)$$

Here Φ_0 is the solution to the zeroth-order problem $H_0\Phi_0 = E_0\Phi_0$, with H_0 constructed with the V^{N-1} one-electron potential.^{5,9} The perturbation H'' in Eq. (3) is

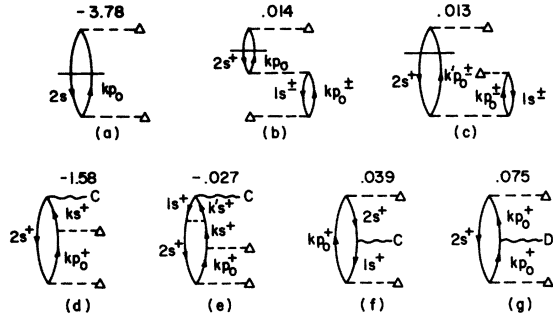


FIG. 1. Leading diagrams for the HSS of Li^7 . Contributions to κ above the diagrams are in units of 10^{-8} Hz/ $(\text{V}/\text{cm})^2$.

$$H'' = \sum_{i>j} \frac{1}{r_{ij}} + \sum_i V_i^{N-1} + H_e, \quad (4)$$

with the Stark Hamiltonian being $H_e = \sum_i e \vec{r}_i \cdot \vec{\epsilon}$ in the presence of $\vec{\epsilon}$.

For the lithium atom in its ground-state configuration $1s^2 2s$, $^2S_{1/2}$, the occupied and unoccupied states were obtained by numerical integration of the one-electron equations for a V^{N-1} potential⁵ due to the $1s^2$ core and the nucleus. In evaluating the magnetic-hyperfine-frequency contributions in Eq. (2) using Eq. (3), the linked perturbation diagrams which make significant contributions to κ for Li^7 are shown in Fig. 1. The symbol Δ in these diagrams denotes the H_e vertex. Similarly, C or D followed by a wiggly line corresponds to the Fermi-contact and spin-dipolar interactions, the orbital interaction being ineffective here. Although, in keeping with the experimental situation,¹ diagrams are presented for the case of electric field and reference magnetic field (determining the spin quantization) parallel, the perpendicular case can also be evaluated by suitably changing the angular factors for the spin-dipolar diagrams.

Diagrams⁹ 1(a)–1(f) represent the most important Fermi-contact contributions to the HSS. These appear to involve the zero and first orders of electron-electron interaction on the perturbation of the wave function by the electric field. However, if one counts the orders of electron-electron interaction *per se*, some of these diagrams, namely, 1(a)–1(c), involve additional orders of electron-electron

interaction which are present even in the absence of the electric field. This fact is explained in Fig. 2, which gives the meaning of the bars in diagrams 1(a)–1(c).

For lithium, diagrams 1(a)–1(c) contribute about 70% of the calculated HSS. Thus, because of the near degeneracy of the $2s$ and $2p$ states for lithium, the $2p$ contribution in the major diagram 1(a) constitutes almost everything (99.7%), with higher excited states contributing only 0.3% of the total. Considering the other class of Fermi-contact diagrams, 1(d) gives a substantial (about 30%) contribution to the HSS and physically it represents the radial expansion of the $2s$ state owing to second-order perturbation by the electric field. In this diagram, the $kp = 2p$ contribution accounts for 84.5% of the total value, the remainder being due to $3p$ and higher states as well as the continuum. The effect of the electric field on $1s$ states is small, as is evident by the contributions from diagrams 1(e) and 1(f) as well as 1(b) and 1(c). This is easily explained by the combination of the small overlap between the $1s$ and $2s$ states and the fact that $1s$ is tightly bound to the nucleus and can therefore be only weakly perturbed by the electric field.

Finally, diagram 1(g) illustrates that a spin-dipolar interaction is possible when the $2s$ is excited to a p state by the electric field. The contribution from this diagram is small (about 1.5%) and opposite in sign to the net Fermi-contact contribution to the shift. Dipolar contributions which are produced from a second-order perturbation of the wave function by H_e were very small. A nuclear-quadrupole interaction is also possible in the presence of the electric field and receives its major contribution to the HSS from a diagram analogous to 1(g). For Li^7 (where $Q < 0$), the quadrupolar HSS effect is of the same sign as the dipolar and about 2.5% of the latter in magnitude.

From the values of the diagrams, one can draw conclusions about the relative importance of contributions from the perturbation of individual one-electron states [diagram 1(a) with bar replaced by Fermi-contact vertex inserted on $2s$ -hole line, as in the first diagram on the right-hand side of Fig.

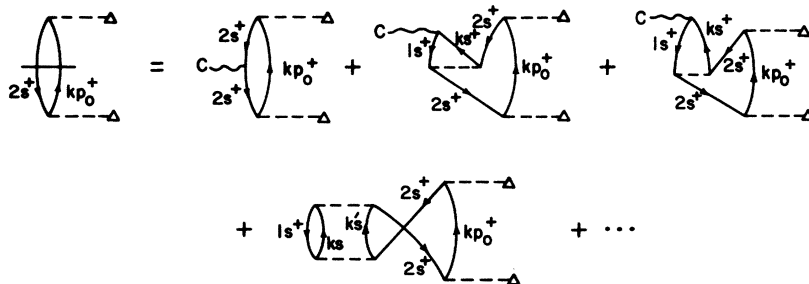


FIG. 2. Significance of the "bar" in the HSS diagrams of Fig. 1.

2, and diagrams 1(d), 1(f), and 1(g)] and those from the additional influence of electron-electron (ee) interactions. The role of ee interactions can be split up further into two parts. The first part involves effects associated with the unperturbed atom, referred to hereafter as zero-field ee effects. The second type of ee effect depends on the presence of the electric field and will be referred to as the Stark-perturbed ee effect. Examples of the latter are represented by diagrams 1(b), 1(c), and 1(e). For the present case of lithium, the net ee interaction contribution is about 20% of the total calculated HSS. This is almost entirely constituted of the zero-field ee effect, owing to the near cancellation of the Stark-perturbed ee effect among 1(b), 1(c), and 1(e).

This examination of the relative contributions from various diagrams and the similarity¹⁰ of the direct, core-polarization, and correlation contributions to the zero-field hyperfine interaction, among the alkali atoms, led us to conclude that the over-all importance of ee results will be quite similar for all of them. As a point of detail, for the other alkali-metal atoms, the influence of the Stark-perturbed ee effect, of course, may not be as negligible as in the present case, because the close cancellations among the class of diagrams 1(b), 1(c), and 1(e) may not recur, especially since we now have *p* shells for the valence-*s* electron to correlate with. However, one does not expect this latter effect to be of determining importance. In the light of this conclusion, one can understand the reasonable agreement between theory and experiment obtained for Cs¹³³ by Feichtner, Hoover, and Mizushima,¹¹ who did not explicitly include ee effects in their calculation. However, the influence of the zero-field ee effect was included indirectly in their treatment through the use of the experimental hyperfine energy, as exemplified by Fig. 2. In addition, continuum excited states were not included in this treatment.¹¹ But this also does not appear to be a major factor in alkali-metal atoms, in view of our observation that the continuum states do not play a major role in lithium [only 15% of diagram 1(d) and a negligible fraction of diagram 1(a)] due to the proximity of the 2*p* excited state and a similar expectation for the other alkali-metal atoms in view of the small *ns-np* separations. On the other hand, without further work this conclusion cannot be extended to the case of other atoms, particularly those involving more than one electron in the valence shell, such as nitrogen and phosphorus, where correlation effects have already been shown⁴ to be of determining importance for hyperfine in-

teraction in the isolated atom.

Our theoretical HSS for Li⁷ leads to a value of κ in Eq. (2) of $-(5.23 \pm 0.3) \times 10^{-8}$ Hz/(V/cm)² for the parallel case and $-(5.35 \pm 0.3) \times 10^{-8}$ Hz/(V/cm)² for the perpendicular case.⁹ The recently measured value for the parallel case is $-(6.1 \pm 0.2) \times 10^{-8}$ Hz/(V/cm)². The mean values of the calculated and experimental results agree within about 14% of the latter. We have included an estimated error range for the calculated value of κ which is primarily due to the numerical techniques associated with the integration of the electric field vertex in Fig. 1(d). An analysis of uncertainties in the continuum-continuum integration in this diagram associated with this vertex led to an uncertainty of not more than 15% of this diagram or 4% of the experimental value. For the large contact diagram 1(a) we estimate an error of no more than about 1% of the experimental value due to numerical techniques. We thus consider our error-range estimate of $\pm 5\%$ or $\pm 0.3 \times 10^{-8}$ Hz/(V/cm)² as a reasonable upper limit for our theoretical result. Because of the relative simplicity of the lithium atom, we feel that no significant diagrams or physical mechanisms have been omitted from consideration.

The present situation of the small but significant difference between theory and experiment for lithium is somewhat similar to that for the hydrogen atom, where one anticipates the best possible agreement between theory and experiment. There are two published theoretical estimates^{3,12} for hydrogen which differ among themselves by 10%. On the experimental side, a recent measurement² leading to a value $-(0.79 \pm 0.08) \times 10^{-9}$ Hz/(V/cm)² has yielded κ about 6% larger than the previous result,¹³ while the range of error has been increased from 6 to 10%. The most recent published theoretical result³ is about 10% different from the latest mean experimental value and just inside the range of experimental error. In view of these observations on hydrogen, it appears to us that additional measurements of the lithium HSS, including a measurement of κ for the perpendicular case, would be very helpful in resolving the small remaining difference with theory. In this connection, it is worth noting that for potassium a difference in mean values of κ of about 10% has been reported between two recent measurements.^{1,14} We are currently in the process of carrying out a theoretical study of κ along the same lines as here to make a comparison with this system.

The authors are grateful to Dr. R. J. Mowat for sending us his results prior to publication.

*Work supported by the National Science Foundation.

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PHYSICAL REVIEW A

VOLUME 8, NUMBER 2

AUGUST 1973

Closed-Form Hydrogenic Radial r^k Matrix Elements and the Factorization Method

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(Received 23 April 1973)

It is shown that the factorization method, when introducing accelerated ladder operators or accelerated ladder matrices, leads to a formula in closed form for the general off-diagonal ($n \neq n'$) hydrogenic r^k matrix elements. This explicit expression, which involves only factorials and binomial coefficients, is directly reducible to any particular case. The well-known selection rules follow from the formula. The method seems appropriate to other cases of factorizable equations. Its extension to the Dirac-Coulomb, generalized Kepler problems, and the discrete-continuous case is considered.

INTRODUCTION

If, for special cases, hydrogenic radial r^k integrals have been calculated many times, either using the generating function of Laguerre polynomials,^{1,2} or using both the factorization method and algebraic manipulations,³ or both the factorization method and group theory,⁴⁻⁷ the evaluation of the general matrix element is known to be rather difficult and intricate, owing to the quantum-number- n dependence of the variable. Recently, we have questioned whether the factorization method is solely able to give recursion formulas or whether it can also give explicit formulas without the help of group theory, and we have shown⁸ that this method, when followed by an "accelerated" operatorial formalism or an equivalent matrix procedure, leads to formulas in closed form for calculating diatomic vibrational-transition matrix elements. While investigating this last question, it appeared that it contained the hydrogenic case with two slight changes: On the one hand, the key matrix elements are trivial, as they merely reduce to factorials or to Euler complex- Γ functions (for the discrete-continuous key matrix elements); on the other hand, one must be careful when normalizing the wave functions.³

A preliminary investigation has shown that the

difficulties for evaluating the diagonal or the off-diagonal matrix elements are of the same kind; in the present paper, we consider, the general ($n \neq n'$) hydrogenic radial r^k integral. Other particular cases are merely a reduction of this last case. In Sec. I the recursion formulas we use are derived. In Sec. II, it is shown how the operator formalism and the alternative matrix procedure work, and we give the hydrogenic radial $\langle nl | r^k | n' l' \rangle$ matrix elements in closed form. The results are given and discussed in Sec. III.

I. RECURSION FORMULAS

The radial Schrödinger equation for a Coulomb field, after setting $\psi_{nl}(r) = r^{-1}R_{nl}(r)$, is

$$\left(\frac{d^2}{dr^2} + \frac{2Z}{r} - \frac{l(l+1)}{r^2} - \frac{Z^2}{n^2} \right) R_{nl}(r) = 0. \quad (1)$$

If one defines $2Zr = e^x$ and $R(r) = e^{x/2}U(x)$, Eq. (1) transforms to

$$\left(\frac{d^2}{dx^2} - \frac{1}{4n^2}e^{2x} + e^x - (l + \frac{1}{2})^2 \right) U(x) = 0. \quad (2)$$

Equation (2) is factorizable,^{3,9} i.e., one can write the following pair of difference-differential equations equivalent to Eq. (2):