Magnetic Hyperfine Structure and Core Polarization in the Excited States of Lithium*

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The magnetic hyperfine splitting constants, a_J, from theoretical calculations on the 3^2S, 2^2P, 3^2P, and 3^2D excited states of the Li atom are reported. The wave functions were calculated using the author's GF method, which corresponds to optimizing the orbitals of a Slater determinant *after* spin projection. Thus the wave functions include core polarization, but no appreciable correlation. For the 2^2P state we calculate $a_{1/2}=0.2206$ a.u. (45.74 Mc/sec for ^{7}Li) which is in good agreement with the experimental value, 0.2227 ± 0.0017 a.u. (46.17 ± 0.35 Mc/sec for ^{7}Li), and the value from configuration interaction calculations, 0.2206. Thus for the Li atom core polarization accounts for most of the error in the Hartree-Fock values of a_J. These calculations yield $\langle 1/r^3 \rangle$ and spin density, $Q(0)$, in agreement with other accurate theoretical calculations, and in disagreement with the values found using level crossing experiments, indicating that the interpretation of the level crossing experiments in terms of $\langle 1/r^3 \rangle$ and $Q(0)$ may not be correct. It is found that for both the unrestricted Hartree-Fock and GF methods the use of a different Hamiltonian for each electron leads to virtual orbitals which are good approximations to the actual orbitals of excited states.

INTRODUCTION

The Fermi contact portion of the magnetic hyperfine interaction is proportional to the spin density at the nucleus, $Q(0)$. The Hartree-Fock (HF) wave function for an atom such as Li $^2P(1s^22p)$, N $^4S(1s^22s^22p^3)$, or O $^3P(1s^22s^22p^4)$ has all s orbitals doubly occupied and hence leads to a zero Fermi contact interaction. However, the experimental results show that the Fermi contact term is *not* zero in these atoms[1,2] and thus that the spin density at the nucleus is nonzero. This clearly indicates that to study such interactions we must improve upon the Hartree-Fock wave function. One approach has been to use configuration interaction (CI),[3,4] where many Slater determinants are formed from a large set of orbitals, and the determinants are combined such as to minimize the total energy. If this is carried out for a complete set of orbitals, we must get the exact wave function, and thus for a sufficiently large basis set we should be able to get arbitrarily good energies and spin densities and correctly account for the magnetic hyperfine interactions.

Another approach has been to retain the Slater determinant form of the wave function, but to remove some of the other restrictions of the Hartree-Fock method. In particular if we allow the 1s orbitals of the Li ^2P wave function to be different for different spins, there will be a net spin density at the nucleus, $|\phi_{1a}(0)|^2 - |\phi_{1b}(0)|^2$, where ϕ_{1a} is associated with α spin and ϕ_{1b} with β spin. This procedure, which is called the unrestricted Hartree-Fock (UHF) method,[5] has the disadvantage[6] that the many electron wave function is not an eigenfunction of $\hat{S}^2$. Since the property we are considering depends on spin, we are led to consider the spin projected UHF (PUHF) wave function in which we delete the parts of the UHF wave function having the wrong spin. However, in this case we are using the orbitals optimized for the unprojected (UHF) function, whereas we really should use the orbitals optimized for the projected function. This latter approach in which the orbitals are optimized after spin projection is equivalent to the GF method[7-9] for electronic wave functions. That is the GF wave function is the best possible spin projected Slater determinant wave function.[7]

Since the GF wave function is based on spin projection of a single Slater determinant, it will not coincide with the exact wave function and will not yield the spin density exactly. However, it does take into account the direct spin polarization of the core (we will call this core polarization) caused by the unpaired spins of the valence electrons. Any difference between the GF value of $Q(0)$ and the exact value could be accounted for by mixing in sufficient other spin projected determinants; such effects we will simply ascribe to correlation. Thus we distinguish the simple exchange correlation involved in core polarization and accounted for by GF wave functions from the other kinds of correlation.

We will see that just as for the Li 2 ^2S ground state[8] the GF wave function also accounts for the hyperfine structure of the Li 2 ^2P state, and thus corrections beyond direct core polarization are not too important for Li.

CALCULATIONS

The 2 ^2S, 3 ^2S, 2 ^2P, 3 ^2P, and 3 ^2D states of Li were considered, and UHF, PUHF, and GF calculations were carried out for each state. Since HF wave functions for these states have been published by Weiss,[4] we used basis sets based upon his calculations. These basis sets of Slater orbitals[10] were selected so as to satisfy the cusp condition at the nucleus [this seems to be important for reliable values of $Q(0)$, especially for larger atoms such as N]. It was established that for Li the optimum orbital exponents for all three types of wave

functions (HF, UHF, and GF) are essentially the same. Four of the ns orbitals were primarily used by the core electrons and had been taken to have the same orbital exponents in all of Weiss's calculations. We reoptimized these orbitals for the $2\,^2P$ state and found that the new orbital exponents also led to lower energies and better virial ratios for the other states. Thus we changed Weiss's basis sets by using these reoptimized (for the $2\,^2P$ state) exponents for the core orbitals.

A self-consistent-field calculation (e.g., HF, UHF, or GF) for the second-lowest state of some symmetry [e.g., $3\,^2P(1s^2 3p)$] is straightforward and leads to an upper bound on the exact energy of the excited state (see Appendix C). However, for the $3\,^2S$ and $3\,^2P$ states of Li the solutions of the usual form of the UHF and GF equations diverged and oscillated. This required using the form of the self-consistent-field equations derived directly from the variational theorem rather than the usual form of the equations in which self-repulsion terms are added. This is discussed later.

CORE POLARIZATION

The calculated hyperfine splitting constants are given in Table I (see Appendix B for the relationships between a_J and $Q(0)$ and $\langle 1/r^3\rangle$). As occurred for the $2\,^2S$ state,[7] the $a_{1/2}$ for $2\,^2P$ as calculated by both the GF and CI[11] methods is in good agreement with experiment.[12] Since the GF results are close to experiment, we see that the main error in the

TABLE I. Hyperfine splitting constants and other properties for the ground and excited states of Li as obtained from GF and other wave functions. E is the total energy, V is the potential energy, $V/2E$ is the virial ratio, $\rho(0)$ is the electron density at the nucleus, and $Q(0)$ is the spin density at the nucleus. All quantities are in atomic units (the hartree is the unit of energy).

	E	$V/2E$	$\rho(0)$	$\langle\sum r^2\rangle$	$Q(0)$	$\langle 1/r^3\rangle$	$a_{L-\frac{1}{2}}$	$a_{L+\frac{1}{2}}$
2^2S HF	-7.432 725	1.000 002	13.8160	18.638	0.1667	...	...	1.396
UHF	-7.432 749	1.000 000	13.8159	18.630	0.2248	...	...	1.883
PUHF	-7.432 767	0.999 999	13.8159	18.630	0.1866	...	...	1.563
GF	-7.432 813	1.000 000	13.8159	18.609	0.2406	...	...	2.016
CI	-7.477 9[a]				0.2249[b]	...	...	1.884
EXP	-7.478 07[c]				0.2313[d]	...	...	1.937
3^2S HF	-7.310 210	0.999 994	13.7080	119.480	0.038 64	...	...	0.3237
UHF	-7.310 212	1.000 002	13.7067	119.470	0.052 53	...	...	0.4401
PUHF	-7.310 213	1.000 000	13.7067	119.469	0.043 35	...	...	0.3632
GF	-7.310 216	1.000 002	13.7067	119.447	0.056 22	...	...	0.4710
EXP	-7.354 10[c]							
2^2P HF	-7.365 069	0.999 995	13.6534	28.716	0.000 00	0.058 48	0.1559	+0.0311
UHF	-7.365 076	1.000 000	13.6535	28.709	-0.017 47	0.058 52	0.2407	-0.0176
PUHF	-7.365 080	1.000 000	13.6535	28.709	-0.005 82	0.058 52	0.1722	+0.0149
GF	-7.365 091	1.000 002	13.6534	28.692	-0.023 04	0.058 61	0.2206	-0.0331
CI	-7.408 38[e]				-0.022 22[f]	[g]	0.2206	-0.0302
EXP	-7.410 16[c]						0.2227[h]	[i]
3^2P HF	-7.293 186	0.999 945	13.6660	172.536	0.00000	0.017 59	0.046 89	+0.009 37
UHF	-7.293 187	0.999 972	13.6661	172.530	-0.005531	0.017 60	0.062 34	-0.006 07
PUHF	-7.293 188	0.999 972	13.6661	172.530	-0.001843	0.017 60	0.052 04	+0.004 22
GF	-7.293 189	0.999 972	13.6661	172.511	-0.007318	0.017 59	0.067 35	-0.011 06
EXP	-7.337 15[c]							
3^2D HF	-7.291 973	0.999 936	13.6715	126.924	0.00000	0.004 951	0.004 948	0.001 412
UHF	-7.291 974	0.999 966	13.6722	126.923	-0.000036	0.004 951	0.005 008	0.001 352
PUHF	-7.291 974	0.999 966	13.6722	126.923	-0.000012	0.004 951	0.004 968	0.001 392
GF	-7.291 974	0.999 966	13.6722	126.923	-0.000053	0.004 951	0.005 037	0.001 323
EXP	-7.335 52[c]							

[a] E. A. Burke, Phys. Rev. 130, 1871 (1963).
[b] E. A. Burke, Phys. Rev. 135, A621 (1964).
[c] Atomic Energy Levels, compiled by C. E. Moore, National Bureau of Standards Circular No. 467 (U. S. Government Printing Office, Washington; D. C., 1947).
[d] P. Kusch and H. Taub, Phys. Rev. 75, 1477 (1949); R. G. Schlect and D. W. McColm, Phys. Rev. 142, 11 (1966). The conversion factor from Mc/sec to a.u. is given in Appendix B.
[e] Weiss, Ref. 4
[f] Ardill and Stewart, Ref. 18.
[g] $\langle 1/r^3\rangle_{\rm orb} = .059\,75$, $\langle 1/r^3\rangle_{\rm dip} = .059\,23$ Ref. 17.
[h] Ritter, Ref. 15.
[i] See discussion in the Core Polarization section.

HF calculations for the magnetic field at the nucleus, $\vec{H}(0)$, is just the lack of core polarization. The error due to correlation is the difference between the GF and experimental values which we see is small.

The $a_{3/2}$ hfs constant for the $2\,^2P$ state could not be measured directly.[12] However, some level crossing experiments were carried out[13,14] which led to effective values of $\langle 1/r^3\rangle$ and $Q(0)$ that could be extrapolated to zero magnetic field in order to calculated $a_{3/2}$. The resulting value for $\langle 1/r^3\rangle$ is 0.0645 a.u. which differs from the CI value[5,15] by about 8%. The CI values of 0.0596 and 0.0594 for the $a_{1/2}$ and $a_{3/2}$ states are consistent with HF, UHF, PUHF, and GF values of 0.0585 to 0.0586 and should be expected to be within 1% of the exact value. Since the CI and GF values of $Q(0)$ and $\langle 1/r^3\rangle$ are consistent with the experimental $a_{1/2}$, it may be that the interpretation of the experimental results in terms of $Q(0)$ and $\langle 1/r^3\rangle$ are incorrect.[15] In particular the external field, H, must lead to perturbations in the core orbitals which depend on H and thus lead to effective values of $Q(0)$ and $\langle 1/r^3\rangle$ which are different for each level and which depend on H.[14] Since the value of $a_{3/2}$ from the GF and CI calculations is a factor of two larger than that extrapolated from level crossing experiments, it may be that direct measurements at small field could determine which of these values is best even though it cannot[12] give a precise value to $a_{3/2}$. (Note from Table I that the HF and PUHF wave functions lead to the wrong sign of $a_{3/2}$ for the Li $2\,^2P$ and $3\,^2P$ states.)

We should note here that since the UHF wave function is not an eigenstate of $\hat{S}^2$ or $\hat{J}^2$, the UHF values for a_J are somewhat suspect since a_J is necessarily defined for some specific value of J. We have used the usual[13,16] (apparently reliable) procedure of pretending that the UHF wave function has the same J and S that it would have if the core orbitals were identical.

Perturbation Approximations

Rather than calculate the effect of core polarization self-consistently as in the GF method, several perturbation approaches (starting with the HF wave function) have been suggested.[17,18] One interesting approach[18] lets the core orbitals be perturbed by the nuclear magnetic moment via the Fermi contact term. By solving for the electronic energy for the perturbed wave functions, one gets directly the core polarization contribution to a_J. Since the orginal perturbation is due to the nuclear moment, the distortion of the core orbitals should be relatively independent of the electronic state. Thus the core polarization in molecules or metals can be calculated more easily. This approach leads to an approximation to the UHF wave function and for the $2s$ and $2p$ states of Li leads to core polarization contributions to $Q(0)$ of 0.0482 and -0.0154, respectively, which are about 85% of the UHF values. Similarly, a perturbation approximation[19] to the GF function for the $2\,^2S$ state yields a core polarization contribution to $Q(0)$ of 81% of the GF value. Thus, self-consistency is important for a reliable value of $Q(0)$.

Summary on Core Polarization

The term core polarization refers only to changes which occur upon improving the wave function within the independent particle interpretation, i.e., as in going from HF to UHF or HF to GF. The GF results given here show clearly the importance of core polarization and thus justify the concept both for polarization by s and non-s electrons.[20] Regardless of how the remaining correlation energy is taken into account, it leads to a minor change in $Q(0)$. By comparing the GF and HF energies, we see that although the core polarization effects are crucially important for $Q(0)$, they have an almost negligible (but numerically significant) effect on the energy, which is the reason that some very good (low-energy) calculations have yielded rather poor spin densities.[21]

CALCULATIONS ON EXCITED STATES

In carrying out calculations on the $3\,^2S$ and $3\,^2P$ excited states of Li, we observed some interesting features which would be expected to occur generally when performing calculations on excited states of the same symmetry as some lower state. In order to keep the discussion clear and simple, we will discuss the $3\,^2S$ state of Li.

In the UHF method for Li we consider a wave function of the form

$$\mathcal{A}[\phi_{1a}(1)\phi_{2a}(2)\phi_{1b}(3)\alpha(1)\alpha(2)\beta(3)],$$

and require that the orbitals be optimum, that is, yield a stationary energy. (In the above expression $\mathcal{A}$ is the antisymmetrizer, and α and β are the spin-up and spin-down eigenfunctions of $\hat{s}_z$.) The result is a set of three equations

$$\begin{aligned} H_{1a}\phi_{1a} &= \epsilon_{1a}\phi_{1a}, \\ H_{2a}\phi_{2a} &= \epsilon_{2a}\phi_{2a}, \\ H_{1b}\phi_{1b} &= \epsilon_{1b}\phi_{1b}, \end{aligned} \tag{1}$$

the self-consistent solutions of which are the optimum orbitals. In (1)

$$\begin{aligned} H_{1a} &= h + \mathcal{J}_{2a} - \mathcal{K}_{2a} + \mathcal{J}_{1b}, \\ H_{2a} &= h + \mathcal{J}_{1a} - \mathcal{K}_{1a} + \mathcal{J}_{1b}, \\ H_{1b} &= h + \mathcal{J}_{1a} + \mathcal{J}_{2a}, \end{aligned} \tag{2}$$

where

$$\mathcal{J}_i(1) = \int dx_2 \phi_i^*(2)\phi_i(2)/r_{12}$$

$$\mathcal{K}_i(1) = \int dx_2 \phi_i^*(2)\hat{P}_{12}\phi_i(2)/r_{12}$$

are the Coulomb and exchange operators and $\hat{P}_{12}$ permutes electrons 1 and 2. However,

$$(\mathcal{J}_i - \mathcal{K}_i)\phi_i = 0.$$

So (2) are usually replaced by

$$H_A = h + (\mathcal{J}_{1a} - \mathcal{K}_{1a}) + (\mathcal{J}_{2a} - \mathcal{K}_{2a}) + \mathcal{J}_{1b}\ ,$$
$$H_B = h - \mathcal{J}_{1a} - \mathcal{J}_{2b} - (\mathcal{J}_{1b} - \mathcal{K}_{1b}), \tag{3}$$

where (3) has the same self-consistent solutions as (2),

$$H_A\phi_{1a} = \epsilon_{1a}\phi_{1a},$$
$$H_A\phi_{2a} = \epsilon_{2a}\phi_{2a}, \tag{4}$$
$$H_B\phi_{1b} = \epsilon_{1b}\phi_{1b}.$$

Besides the self-consistent solutions (i.e., the ones used in the field terms), (2) and (3) have an infinite number of other solutions, called the virtual orbitals. Let us consider the ground state of Li, $2\,^2S[(1s)^2(2s)]$. Then $1a$ and $1b$ correspond to $1s$ orbitals and $2a$ corresponds to the $2s$ orbital. From (1) and (2) we have

$$\epsilon_{2a} = \langle\phi_{2a}|h|\phi_{2a}\rangle + \mathcal{J}_{1a,2a} - \mathcal{K}_{1a,2a} + \mathcal{J}_{1b,2a}\ , \tag{5}$$

where

$$\mathcal{J}_{1a,2a} = \langle\phi_{2a}|\mathcal{J}_{2a}|\phi_{1a}\rangle = \langle\phi_{2a}(1)\phi_{1a}(2)|1/r_{12}|\phi_{2a}(1)\phi_{1a}(2)\rangle$$

$$\mathcal{K}_{1a,2a} = \langle\phi_{2a}|\mathcal{K}_{1a}|\phi_{2a}\rangle = \langle\phi_{2a}(1)\phi_{1a}(2)|1/r_{12}|\phi_{1a}(1)\phi_{2a}(2)\rangle.$$

Hence (5) is just the difference in energy between the three-electron wave function $\mathcal{A}(\phi_{1a}\phi_{2a}\phi_{1b}\alpha\alpha\beta)$ and the two-electron wave function $\mathcal{A}(\phi_{1a}\phi_{1b}\alpha\beta)$, and thus (5) is expected to be close to the ionization energy for the $2s$ electron (Koopmans' theorem[22]). Now consider the solution of H_{2a} which has two nodes and is spherically symmetric (i.e., the $3s$ virtual orbital), and call this orbital $\phi_{3s}{}^{2a}$

$$H_{2a}\phi_{3s}{}^{2a} = \epsilon_{3s}{}^{2a}\phi_{3s}{}^{2a}. \tag{6}$$

Then from (2) and (6)

$$\epsilon_{3s}{}^{2a} = \langle\phi_{3s}|h|\phi_{3s}\rangle + \mathcal{J}_{1a,3s} - \mathcal{K}_{1a,3s} + \mathcal{J}_{1b,3s}\ , \tag{7}$$

which is just the difference between the energy of the three-electron wave function $\mathcal{A}(\phi_{1a}\phi_{3s}{}^{2a}\phi_{1b}\alpha\alpha\beta)$ and that of the two-electron wave function $\mathcal{A}(\phi_{1a}\phi_{1b}\alpha\beta)$. Thus (7) is expected to close to the ionization energy for a $3s$ electron, and the virtual solutions of H_{2a} can be expected to be good approximations to the excited state orbitals of the Li atom.

Now consider the $3s$ virtual solution of H_A

$$H_A\phi_{3s}{}^{A} = \epsilon_{3s}{}^{A}\phi_{3s}{}^{A}\ .$$

From (3) this has an energy of

$$\epsilon_{3s}{}^{A} = \langle\phi_{3s}|h|\phi_{3s}\rangle + \mathcal{J}_{1a,3s} - \mathcal{K}_{1a,3s} + \mathcal{J}_{1b,3s} + \mathcal{J}_{2a,3s} - \mathcal{K}_{2a,3s}\ .$$

But the ionization potential for the $3s$ electron should be as in (7); thus $\epsilon_{3s}{}^{A}$ is too large by $\mathcal{J}_{2a,3s} - \mathcal{K}_{2a,3s}$, which is just the term arising from the addition of the self-Coulomb and exchange operators to H_{2a}. Since $\mathcal{J}_{2a,3s} > \mathcal{K}_{2a,3s}$ the energies of the A-type virtual orbitals are all to high (in the case of the Li atom ground state, the virtual orbitals are all unbound), and the orbitals are too diffuse. This occurs because the virtual orbitals see an effective field due to N other electrons rather than N-1 other electrons. (The $\phi_{3s}{}^{A}$ virtual orbital of H_A is an approximation to the ϕ_{3s} in $\mathcal{A}(\phi_{1a}\phi_{2a}\phi_{3s}\phi_{1b}\alpha\alpha\alpha\beta)$, which is a wave function for the $3\,^3S$ state of Li^-, probably an unstable state.)

To illustrate these points, both (1) and (4) were solved for the ground state of Li using a basis set of 15 basis functions. The resulting eigenvalue spectra are given in Table II, where they are compared with the experimental and self-consistent-field values for the excited states. We see that the virtual solutions of H_{2a} are comparable to the self-consistent solutions for the excited states, whereas this is not at all true for the virtual solutions of H_A. The errors in the higher eigenvalues of H_{2a} are mainly due to the incompleteness of the basis set. If a complete basis set had been used, we probably would have obtained good values for the energies of all observed ns, np, nd, and nf states of Li. Thus if one wishes to study a series of rydberg states of an atom or molecule without doing each state self-consistently, the HF or UHF equations analogous to (1) should be used, rather than those analogous to (4). Actually, the core orbitals can be solved for with (3) as long as the orbital to be excited is solved for with the H_i from (2).

If we wish to solve self-consistently for the $(1s)^2(3s)\,^2S$ excited state of Li, we just solve (1) where the ϕ_{2a} in $\mathcal{J}_{2a}$ and $\mathcal{K}_{2a}$ is taken to be the third lowest s solution to H_{2a} rather than the second lowest. As would be expected, this process works well, and the wave functions converge as well as for the ground state. We could also use the same process with (4) where we would take the first and third solutions of H_A to be occupied. However, in this case the second and third s-type solutions are nearly degenerate, and the iteration process diverges (this problem also occurs for the $3\,^2P$ state of Li). Thus we were forced to use (1) for

TABLE II. The energies for the $2s$ orbitals and the virtual orbitals of Li from UHF and GF calculations (the basis set was based on the effective quantum numbers, n^*, from the term values of the lower s and p states. We used $1s$, $2s=2.7$; $2s$, $3s=0.63$; $3s$, $4s=0.39$; $4s$, $5s=0.28$; $5s=0.22$; $2p$, $3p=0.51$; $3p$, $4p=0.34$; $4p$, $5p=0.25$ where the Slater orbital is represented by nl and the number is the orbital exponent) on the ground state, $^2S[(1s)^2(2s)]$. Energies are in hartrees.

	UHF		GF			
State	H_{2a} Different[c] Hamiltonian	H_A Same[d] Hamiltonian	H_{2a} Different[c] Hamiltonian	H_A Same[d] Hamiltonian	SCF[a]	Experimental[b]
$2s$	-0.1961	-0.1961	-0.1963	-0.1963	-0.1963	-0.1982
$3s$	-0.0738	+0.0017	-0.0738	-0.0152	-0.0738	-0.0742
$4s$	-0.0385	+0.0077	-0.0385	-0.0060	...	-0.0386
$5s$	-0.0236	+0.0214	-0.0236	+0.0033	...	-0.0236
$6s$	-0.0123	+0.0548	-0.0123	+0.0289	...	-0.0159
$2p$	-0.1283	+0.0036	-0.1283	-0.0273	-0.1287	-0.1302
$3p$	-0.0567	+0.0106	-0.0567	-0.0084	-0.0568	-0.0572
$4p$	-0.0317	+0.0230	-0.0317	+0.0005	...	-0.0320
$5p$	-0.0193	+0.0516	-0.0193	+0.0221	...	-0.0204

[a]To this many places the UHF and GF methods yield the same orbital energies.

[b]Experimental excitation energies from C. Moore, footnote c to Table I. This column is not strictly comparable with the other columns because of differences in the core states and correlation energy for the various states. However, these differences are small for the excited states.

[c]No self-repulsion terms are included in the one-electron Hamiltonian. Thus each electron has a different Hamiltonian.

[d]Self-repulsion terms are included in the one-electron Hamiltonian. Thus ϕ_{1a} and ϕ_{2a} are both eigenstates of the same Hamiltonian.

calculations on these excited states of Li.

All these results are exactly the same in the GF case. The wave function is taken as

$$G_f(\phi_{1a}\phi_{2a}\phi_{1b}\alpha\alpha\beta),$$

and the equations for the optimum orbitals are as in (1), [7,9] where the forms of H_{1a}, H_{2a}, and H_{1b} are more complicated than (2). For example, after making a Roothaan expansion of the orbitals in terms of basis functions $\{X_\mu\}$ the matrix equivalent of H_{2a} has the form[7,9,23]

$$\begin{aligned}
H_{\mu\nu}^{2a} &= (1+\tfrac{1}{2}\langle 1a\,|\,1b\rangle^2)\langle\mu\,|h|\,\nu\rangle \\
&+\tfrac{1}{2}(\langle\mu\,|h|\,1b\rangle-\langle\mu\,|h|\,1a\rangle\langle 1a\,|\,1b\rangle)\langle 1b\,|\,\nu\rangle \\
&+\tfrac{1}{2}\langle\mu\,|\,1b\rangle(\langle 1b\,|h|\,\nu\rangle-\langle 1a\,|h|\,\nu\rangle\langle 1b\,|\,1a\rangle) \\
&+\tfrac{1}{2}\langle\mu\,|\,1b\rangle\langle 1b\,|\,\nu\rangle(\langle 1a\,|h|\,1a\rangle-E) \\
&+(\mu\nu\,|\,1a1a)+(\mu\nu\,|\,1b1b)+(\mu\nu\,|\,1a1b)\langle 1a\,|\,1b\rangle \\
&-(\mu 1a\,|\,\nu 1a)+\tfrac{1}{2}(\mu 1b\,|\,\nu 1b) \\
&-\tfrac{1}{2}\langle 1a\,|\,1b\rangle[(\mu 1a\,|\,\nu 1b)+(\mu 1b\,|\,\nu 1a)] \\
&+\tfrac{1}{2}[(\mu 1b\,|\,1a1a)-(\mu 1a\,|\,1a1b)]\langle 1b\,|\,\nu\rangle \\
&+\tfrac{1}{2}\langle\mu\,|\,1b\rangle[(1a1a|\,\nu 1b)-(1a1b\,|\,\nu 1a)].
\end{aligned}$$

Again we can add terms to H_{1a} and H_{2a} to get an H_A such that ϕ_{1a} and ϕ_{2a} are both solutions of H_A as in (4). For example, we would add

$$\begin{aligned}
\Delta H_{\mu\nu}^{2a} &= \tfrac{1}{2}\langle 2a\,|\,1b\rangle^2\langle\mu\,|h|\,\nu\rangle \\
&-\tfrac{1}{2}\langle\mu\,|h|\,2a\rangle\langle\,2a\,|\,1b\rangle\langle 1b\,|\,\nu\rangle \\
&-\tfrac{1}{2}\langle\mu\,|\,1b\rangle\langle 1b\,|\,2a\rangle\langle 2a\,|h|\,\nu\rangle \\
&+\tfrac{1}{2}\langle\mu\,|\,1b\rangle\langle 1b\,|\,\nu\rangle\langle 2a\,|h|\,2a\rangle \\
&+(\mu\nu\,|\,2a2a)+(\mu\nu\,|\,2a1b)\langle 2a\,|\,1b\rangle \\
&-(\mu 2a\,|\,\nu 2a) \\
&-\tfrac{1}{2}\langle\,2a\,|\,1b\rangle[(\mu 2a\,|\,\nu 1b)+(\mu 1b\,|\,\nu 2a)] \\
&+\tfrac{1}{2}[(\mu 1b\,|\,2a2a)-(\mu 2a\,|\,2a1b)]\langle 1b\,|\,\nu\rangle \\
&+\tfrac{1}{2}\langle\mu\,|\,1b\rangle\,[(2a2a\,|\,\nu 1b)-(2a1b\,|\,\nu 2a)]
\end{aligned}$$

to $H_{\mu\nu}^{2a}$ to get $H_{\mu\nu}^{A}$. (Note that $\sum_\nu \Delta H_{\mu\nu}^{2a} \times\langle\nu\,|\,2a\rangle=0$.) Just as in the UHF case, we find that the virtual solutions of H_{2a} are good approximations to the excited orbitals, whereas the virtual solutions to H_A are not (see Table II).

Of course the above results apply equally well to other symmetries and other systems of various numbers of electrons.

DEPENDENCE OF PROPERTIES UPON EXCITED STATES

The total electronic density at the nucleus, $\rho(0)$, is given in Table III for the various states of Li. It is interesting to note that for ns states the $\rho(0)$ decreases as we go to large n, eventually decreasing to the $\rho(0)$ of Li^+, but that for np and nd states $\rho(0)$ is less than the $\rho(0)$ of Li^+ and increases to $\rho(0)$ of Li^+ as n and l increase.[24] An explanation of this behavior is that the valence electron, nl, partly shields the nucleus from the core electrons and thus leads to a slightly lower contribution to $\rho(0)$ from the core electrons, $\rho(0)_{core}$, as compared to Li^+. If the added electron is in an ns state, it has a nonzero amplitude at the nucleus which leads to an increase in $\rho(0)$ that more than cancels the previous decrease. But for $l \neq 0$ there is no compensating term, and $\rho(0)$ is lower for the atom than for Li^+. (Note that $\rho(0)_{core}$ is nearly independent of l for ns and np states.)

In addition, (see Table I) we have the order $2s < 2p < 3s < 3p < 3d$ for total energy, whereas for $\langle \sum r^2 \rangle$ we have the order $2s < 2p < 3s < 3d < 3p$. Thus using $\langle \sum r^2 \rangle$ as the criterion, ϕ_{3d} is less diffuse than ϕ_{3p}, but more diffuse than ϕ_{3s}. However, for $\langle 1/r^3 \rangle_{nl}$ the order is $2p < 3p < 3d$, which might be expected since the inner loop of the $3p$ should count heavily here.

The value of $\langle 1/r^3 \rangle$ for various states nl of the same l are often[25,26] expected to scale as $(1/n^*)^3$, where n^* is the effective quantum to use in the hydrogen atom formula in order to obtain the term energy. It has been less clear how the spin density term would scale, although it has also been assumed[26] to scale as $(1/n^*)^3$. In Table IV we compare the scaling of the hyperfine constants to that of n^*. We see that $(1/n^*)^3$ leads to results too small by 1% and 8% for $Q(0)$ of the $3\,^2S$ and $3\,^2P$ states and too small by 2%, 4%, and 13% for $\langle 1/r^3 \rangle$, $a_{1/2}$ and $a_{3/2}$ of the $3\,^2P$ state.

CONCLUSIONS

For the excited states of Li as for the ground state, the GF wave function leads to good values for the hyperfine parameters. Thus the major error in the Hartree-Fock value of the hyperfine splitting constants of Li is due to the lack of core polarization.

TABLE III. The density at the nucleus, $\rho(0)$, for Li^+ and several states of Li. $\rho(0)_{core}$ is the density at the nucleus due to the $1s$ electrons. The Hartree-Fock wave functions of Weiss (see Ref. 4) for Li and Roothaan, Sachs, and Weiss [Rev. Mod. Phys. 32, 186 (1960)] for Li^+ were used.

	$\rho(0)$	$\rho(0)_{core}$
Li 2^2S	13.816	13.652
3^2S	13.708	13.666
2^2P	13.653	13.653
3^2P	13.666	13.666
3^2D	13.672	13.672
Li^+ 1^1S	13.674	13.674

The calculated $a_{3/2}$ from GF and CI calculations disagree with the values deduced from the level-crossing experiments. This casts doubt on the interpretation of these experiments in terms of effective $\langle 1/r^3 \rangle$ and $Q(0)$ that are independent of magnetic field.

The use of different Hamiltonians for different orbitals leads to improved convergence of excited-state wave functions and also leads to virtual orbitals closely related to the orbitals of other excited states.

APPENDIX A. THE CALCULATED WAVE FUNCTIONS

The calculated orbitals for the UHF and GF wave functions are available upon request. The basis functions (which are Slater orbitals), the orbital energies (ϵ_i), and the amplitude at the nucleus [$\phi_i(0)$] are given in Table V.

APPENDIX B: HYPERFINE SPLITTING CONSTANTS

We define the hyperfine splitting constant, A_J, as the proportionality constant between $\langle \vec{I} \cdot \vec{J} \rangle$ and the perturbation energy $E = A_J \langle \vec{I} \cdot \vec{J} \rangle$. Then we define a_J by $A_J = g_S \mu_B g_N \mu_N a_J$, where μ_B and μ_N are the Bohr and nuclear magnetons, and g_S and g_N are the gyromagnetic ratios for the electron and nucleus. If the different states are all taken to be eigenstates of $\hat{L}^2$ and $\hat{S}^2$, then a_J is[27]

TABLE IV. The scaling of the hyperfine constants for the ns and np states of Li ($n = 2, 3$). n^* is the effective quantum number obtained from the term energies (from Moore, footnote c to Table I).

	n^*	$(1/n^*)^3$	$Q(0)$	$\langle 1/r^3 \rangle$	$a_{1/2}$	$a_{3/2}$
$2s$	1.588[a]	...	0.2406	...	...	...
$3s$	2.596[a]	...	0.056 22	...	...	...
ratio	...	0.229	0.234	...	...	...
$2p$	1.966[a]	...	−0.023 04	0.058 61	0.2206	−0.033 13
$3p$	2.956[a]	...	−0.007 318	0.017 60	0.067 35	−0.011 06
ratio	...	0.294	0.318	0.300	0.305	0.334

TABLE V. The orbital energy and amplitude at the nucleus from the UHF and GF wave functions of Li. All quantities are in Hartree atomic units. Basis sets: the entries represent the $nl\zeta$ of each Slater orbital (see Ref. 10).

State		Orbital Energy			Amplitude at the Nucleus		
		ϵ_{1a}	ϵ_{1b}	ϵ_{2a}	$\phi_{1a}(0)$	$\phi_{1b}(0)$	$\phi_{2a}(0)$
2^2S[a]	UHF	-2.486 70	-2.468 73	-0.196 37	2.618 48	2.606 84	-0.404 86
	GF	-2.498 75	-2.463 88	-0.196 49	2.633 88	2.591 73	-0.401 95
3^2S[a]	UHF	-2.664 84	-2.660 74	-0.073 80	2.615 54	2.612 87	-0.196 41
	GF	-2.667 66	-2.659 52	-0.073 80	2.619 22	2.609 20	-0.196 12
2^2P[b]	UHF	-2.531 33	-2.530 05	-0.128 68	2.611 13	2.614 48	0.000 00
	GF	-2.530 55	-2.532 20	-0.128 72	2.606 14	2.619 41	0.000 00
3^2P[c]	UHF	-2.677 80	-2.677 35	-0.056 78	2.613 49	2.614 54	0.000 00
	GF	-2.677 55	-2.677 99	-0.056 78	2.611 91	1.616 11	0.000 00
3^2D[d]	UHF	-2.681 23	-2.681 23	-0.055 56	2.614 59	2.614 60	0.000 00
	GF	-2.681 22	-2.681 24	-0.055 56	2.614 58	2.614 61	0.000 00

[a] $1s$ 3.0, $3s$ 8.7, $3s$ 3.398, $3s$ 2.544, $3s$ 1.24, $3s$ 0.757, $3s$ 0.345, $4s$ 0.345.
[b] $1s$ 3.0, $3s$ 8.7, $3s$ 3.398, $3s$ 3.544, $2p$ 1.5, $4p$ 2.12, $4p$ 1.275, $4p$ 0.785, $4p$ 0.566.
[c] Same as b except that $4p$ 0.566 is replaced by $4p$ 0.63, $4p$ 0.37, $4p$ 0.21.
[d] s orbtials as in b, $3d$ 1.0, $5d$ 0.98, $5d$ 0.60, $5d$ 0.404, $5d$ 1.762.

$$a_J=\left(\frac{2}{g_S}\right)a_l\frac{\langle\vec{L}\cdot\vec{J}\rangle}{J(J+1)}+\frac{8\pi}{3}a_c\frac{\langle\vec{S}\cdot\vec{J}\rangle}{J(J+1)}$$
$$+a_d\frac{3\langle\vec{S}\cdot\vec{L}\rangle\langle\vec{L}\cdot\vec{J}\rangle-L(L+1)\langle\vec{S}\cdot\vec{J}\rangle}{J(J+1)}\ .$$

Relativistic effects and breakdown of LS coupling have been ignored and $g_l=1$ has been assumed. The constants in the above equation are defined as

$$a_l=\frac{1}{L}\left\langle LSLS\left|\sum_e\frac{\hat{l}_z}{r^3}\right|LSLS\right\rangle,$$
$$a_c=\frac{1}{S}\left\langle LSLS\left|\sum_e\delta(r)\hat{s}_z\right|LSLS\right\rangle,$$
$$a_d=\frac{1}{SL(2L-1)}\left\langle LSLS\left|\sum_e\left(\frac{3z^2-r^2}{r^5}\right)\hat{s}_z\right|LSLS\right\rangle,$$
$$\langle\vec{L}\cdot\vec{J}\rangle\equiv\tfrac{1}{2}[J(J+1)+L(L+1)-S(S+1)],$$
$$\langle\vec{S}\cdot\vec{J}\rangle\equiv\tfrac{1}{2}[J(J+1)+S(S+1)-L(L+1)],$$
$$\langle\vec{S}\cdot\vec{L}\equiv\tfrac{1}{2}[J(J+1)-S(S+1)-L(L+1)],$$

where $|LSM_LM_S\rangle$ denotes a many-electron wave function having quantum numbers L, S, M_L, and M_S. The subscripts l,c, and d refer to orbital, Fermi contact, and spin-dipolar contributions, respectively.

For the HF, PUHF, and GF wave functions of Li, a_l and a_d simplify since

$$\left\langle LSLS\left|\sum_e\frac{\hat{l}_z}{r^3}\right|LSLS\right\rangle=\left\langle\frac{1}{r^3}\right\rangle$$

and

$$\frac{1}{S}\left\langle LSLS\left|\sum_e\frac{(3z^2-r^2)}{r^5}\hat{s}_z\right|LSLS\right\rangle=\frac{-2l}{(2l+3)}\left\langle\frac{1}{r^3}\right\rangle,$$

where $\langle 1/r^3\rangle$ is a one-electron radial integral over the $l\neq 0$ orbital (with $m_l=l$).

Using the values[28] $g_S=2.002\,3192$, $\mu_B=9.2732\times10^{-24}$ A m^2, $\mu_N=5.050\,50\times10^{-27}$ A m^2, 1 eV $=1.602\ 10\times10^{-19}$J, 1eV $=2.418\,04\times10^{14}$Hz, and $a_0=0.529\ 167$ Å, we find that to convert a_J from atomic units to Mc/sec we have to multiply by $c=95.519_{75}g_N$. Thus for Li^7 using[29] $g_N=3.256\ 31/1.5$, we obtain $c(\mathrm{Li}^7)=207.36_1$.

Using the above equations and letting $a_c\equiv Q(0)$ we obtain

for ns^2S states: $a_{1/2}=8.3776Q(0)$,

for np^2P states: $a_{1/2}=2.6651\langle 1/r^3\rangle-2.7925Q(0)$,

$$a_{3/2}=0.53256\langle 1/r^3\rangle+2.7925Q(0),$$

for nd^2D states: $a_{3/2}=0.99930\langle 1/r^3\rangle-1.6755Q(0)$,

$$a_{5/2}=0.28525\langle 1/r^3\rangle+1.6755Q(0).$$

In the derivation it is necessary to assume that the wave functions are eigenfunctions of L^2 and S^2 and can be combined into eigenfunctions of J^2. This is correct for the HF, PUHF, and GF wave functions for Li, but not for the UHF wave functions. Thus in the UHF case it is not correct to use the above equations (or any others for that matter) for a_J, since the UHF wave functions are not eigenfunctions of S^2 or J^2. However, we will follow the usual practice of using the above equations for UHF also.

APPENDIX C: UPPER BOUNDS ON THE ENERGY FOR EXCITED STATES

The UHF and GF wave functions for the excited states of Li lead to upper bounds on the exact energy, even though the wave functions are not orthogonal to the ground state. Below we sketch the proof of this for GF wave functions.[30] A similar theorem for HF wave functions has been proved using a different approach by Perkins.[31]

Let $\psi_1 = G_f(\phi_{1s}{}^a \phi_{2s}{}^a \phi_{1s}{}^b \alpha\alpha\beta)$,

$$\psi_2 = G_f(\phi_{1s}{}^a \phi_{3s}{}^a \phi_{1s}{}^b \alpha\alpha\beta), \tag{C-1}$$

and consider linear combinations

$$\psi = C_1\psi_1 + C_2\psi_2 \tag{C-2}$$

of these functions. If the coefficients in (C-2) are chosen to make the total energy stationary, we find that the coefficients for the ith solution satisfy

$$\sum_k \langle \psi_j | H - E_i | \psi_k \rangle C_j = 0. \tag{C-3}$$

In addition, from the Hylleraas-Undheim-Mac Donald theorem[32] the calculated energy of the ith solution is an upper bound on the exact energy for the ith solution allowed by the symmetries of (C-1). But if the orbitals in (C-1) are solutions of the GF equations corresponding to (1), where $\phi_{1s}{}^a$, $\phi_{1s}{}^b$, and $\phi_{3s}{}^a$ are used in the field terms, then from the Brillouin theorem for GF wave functions,[33] we have that

$$\langle \phi_{1s}{}^a \phi_c \phi_{1s}{}^b | H - E_2 | O_{ff} \phi_{1s}{}^a \phi_{3s}{}^a \phi_{1s}{}^b \rangle$$
$$= \langle \phi_c | H_{2a}{}^{GF} | \phi_{3s}{}^a \rangle = \epsilon_{3s}{}^a \langle \phi_c | \phi_{3s}{}^a \rangle = 0 \tag{C-4}$$

for any ϕ_c orthogonal to $\phi_{3s}{}^a$. Thus the solutions of (C-3) are $C_1 = 1$, $C_2 = 0$ and $C_1 = 0$, $C_2 = 1$; that is, the ψ_1 and ψ_2 in (C-1) are solutions of (C-3). But[32]

$$E_1 = \langle \psi_1 | H | \psi_1 \rangle / \langle \psi_1 | \psi_1 \rangle = E^* + \epsilon_{2s}{}^a,$$

$$E_2 = \langle \psi_2 | H | \psi_2 \rangle / \langle \psi_2 | \psi_2 \rangle = E^* + \epsilon_{3s}{}^a,$$

where E^* is the part of the energy term which depends only on ϕ_{1a} and ϕ_{1b}, $\epsilon_{3s}{}^a$ is the eigenvalue for the occupied orbital $\phi_{3s}{}^a$, and $\epsilon_{2s}{}^a$ is the eigenvalue of the virtual orbital $\phi_{2s}{}^a$. Thus if $\epsilon_{2s}{}^a < \epsilon_{3s}{}^a$, then $E_1 < E_2$ and ψ_2, the GF solution for the 3^2S state of Li, yields an upper bound on the exact energy of the 3^2S state. This occurs despite the fact that ψ_2 is not orthogonal to the exact GF solution for the 2^2S state and *a fortiori* is not orthogonal to the exact solution of the 2^2S state.

Now consider the case where the N-electron wave function ψ_n is a self-consistent GF solution of the nth state of a given symmetry and $\psi_j (j < n)$ are constructed by replacing $\phi_{ns}{}^a$ by $\phi_{js}{}^a$, a lower energy virtual orbital of H_{2a}. Then (C-4) still holds for $\phi_c = \phi_{js}{}^a$ if $j \neq n$, and ψ_n is already a solution of the equations corresponding to (C-3). Thus if there are $n-1$ virtual orbitals of lower energy, then $E_n = \langle \psi_n | H | \psi_n \rangle / \langle \psi_n | H | \psi_n \rangle$ is an upper bound on the energy of the n^{th} state of this symmetry. This proof does not depend on the symmetry of the valence orbitals; it applies only to excited states obtained by exciting a single electron.

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$$(\alpha\beta|\gamma\delta) = \int d\vec{x}_1 \phi_\alpha{}^*(1)\phi_\beta(1) \times \int d\vec{x}_2 (1/r_{12})\phi_\gamma{}^*(2)\phi_\delta(r)$$

is the usual notation for a two-electron integral. We have multiplied (4) by $(1+\frac{1}{2}\langle 1a|1b\rangle^2)$ for convenience.

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Relativistic Calculations of Electron Binding Energies by a Modified Hartree-Fock-Slater Method

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Relativistic atomic wave functions and electron binding energies have been calculated by a modified Hartree-Fock-Slater method. The local exchange approximation, originally introduced by Slater, is modified in such a way that the total energy of the system is minimized. Approximate expressions for the optimum exchange potential are suggested for all atoms and ions. The total atomic energies and electron binding energies obtained by this method agree extremely well with the corresponding Hartree-Fock results in the cases where such data are available. Various corrections to the theoretical binding energies are discussed, in particular the effect of rearrangement during the ionization process. It is found that this effect is of importance for inner shells in all elements and is responsible for the main discrepancy between experimental and previous theoretical results for light and medium-heavy elements. For heavy elements other effects are of importance, and various possible sources of the residual discrepancy between theory and experiments are discussed.

I. INTRODUCTION

During the last decade our knowledge of electron binding energies in atoms has increased considerably, due in particular to the development of the electron-spectroscopic method (ESCA) by Siegbahn *et al.*[1] This method has been applied to almost all elements between lithium and berkelium and to inner as well as outer shells. The accuracy of the new data is so high that improved theoretical calculations are justified. The electron binding energies are often used to check the accuracy of electronic wave functions. When the accuracy of the calculations increases, several effects have to be taken into account. Besides the relativistic effects, which of course are dominant for heavy elements, it is necessary to consider relaxation mechanisms, correlation effects, core polariza-