Penny is good except at 10 deg for 120 keV, where the experiment is about 20% high. The Born-approximation values as expected are low at the higher photon energies.

The comparisons between experiment and the values from the modified program of Brysk, Zerby, and Penny at 0.20 MeV show some of the same features as those reported by them for the 0.18-MeV data for photon energies of about the same percent of the end point. A tendency for the theory to fall below the experimental values at small angle was also reported by them. However, the discrepancy is considerably less in the present comparison. The difference would have to be primarily due to differences in the experimental values since alterations in the program which were made had little effect on the computed values for Au for 0.20-MeV incident-electron energy at photon energies greater than 20% of the end-point value. In Fig. 7 are shown the data of Aiginger[4] for an incident-electron energy of 0.18 MeV and a photon energy of 0.108 MeV, or 60% of the end-point energy, compared with several computed curves and the present experimental values for an incident energy of 0.20 MeV and a photon energy of 0.12 MeV, also 60% of the end-point energy. The theoretical curves for an incident-electron energy of 0.18 MeV include the curve from the paper by Tseng and Pratt,[7] which apparently does not include screening, and curves from evaluations of the Brysk, Zerby, and Penny formulas with and without screening. Also shown is a curve from the Brysk-Zerby-Penny program with screening for an incident-electron energy of 0.20 MeV and a photon energy of 0.12 MeV, or 60% of the end point. The experimental values of Aiginger are somewhat lower than those shown in the paper of Brysk, Zerby, and Penny. Those shown here were obtained from the graphs of Aiginger by enlarging the figure and superimposing a grid on the enlargement. Otherwise, the experimental values are difficult to read accurately. The two experiments appear to be consistent in that both agree with the calculations with screening from the work of Zerby, Brysk, and Penny at angles greater than about 20 deg and both are high at smaller angles. However, both calculations without screening for an incident energy of 0.18 MeV are in agreement at angles greater than 45 deg while the Brysk-Zerby-Penny values are lower at forward angles. If the values of Tseng and Pratt are affected as much by the inclusion of screening as the Brysk-Zerby-Penny calculations, they should be very close to the experiment at all angles for which measurements have been reported.

Additional values by Tseng and Pratt are of interest especially for higher electron energies where additional experimental values are available.

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PHYSICAL REVIEW A VOLUME 2, NUMBER 6 DECEMBER 1970

Theoretical Evaluation of the Fractional Hyperfine Pressure Shift of Paramagnetic Atoms in a Noble Gas*

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(Received 29 July 1970)

The fractional hyperfine pressure shift (known as HPS in the literature) of paramagnetic atoms in an atmosphere of noble-gas atoms has been found to be computable quite adequately from recently evaluated extended-basis-set self-consistent-field molecular-orbital wave functions. The actual computation was carried out for lithium and sodium atoms in a helium buffer gas. Computed values of 78.87×10^{-9}/mm Hg versus the experimental value of 77.7×10^{-9}/mm Hg for LiHe and 78.11 versus 73.0×10^{-9}/mm Hg for NaHe were obtained.

1. INTRODUCTION

The quantitative evaluation of the fractional HPS of paramagnetic atoms in an inert-buffer-gas atmosphere has been a challenging problem for some time. Until recently, all the attempts that have been made by several investigators[1–5] on systems such as H-He and N-He met with limited success. Qualitative features were explained well, but the quantitative results were poor when compared with experiment. Since the origin of the HPS has been analyzed as arising from the competition between short-range Pauli exclusion effects and long-range polarization effects, the calculation has been divided into two segments, one designed for the short range and the other for the long range. However, serious problems arise when the two calculations are matched at some intermediate value of the internuclear separation, where both effects are of comparable magnitude. The calculated HPS's were found to be too sensitive to the choice of the junction point. In order to avoid these difficulties, we have used recently evaluated molecular-orbital self-consistent-field (MO-SCF) wave functions of near–Hartree-Fock quality calculated over a range of internuclear separations.

It might be argued that electron correlation would be important in the evaluation of the HPS; however, a previous study[6] of the interaction of a hydrogen atom with a helium atom was carried using the method of optimized valence configuration (OVC).[7] The OVC method is a multiconfigurational self-consistent-field technique which mixes near–Hartree-Fock ground states with dispersion states (predominantly states referring to dipole-dipole interactions) and adequately reproduces the interaction energy over almost the entire range of internuclear separation. This wave function did produce the correct change in electronic spin density at the hydrogen nucleus and gave excellent agreement between the calculated and experimental values of the fractional HPS for hydrogen in a helium atmosphere. However, with the exception of the smaller internuclear distances, the contribution of the polarization states to the OVC wave function was small, so that it appeared to a good degree of accuracy that only the primary, or near-Hartree-Fock, configuration need be considered in calculating the change in spin density at the hydrogen nucleus. The increased contribution of the polarization states at small distances is of little consequence in the HPS calculation because of the presence of a Boltzmann term which rapidly goes to zero as the internuclear distance decreases.

Based on the above considerations, we have examined the Li-He and Na-He systems for which near-Hartree-Fock wave functions have been recently evaluated.[8] It is our objective in this paper to show the capabilities and potentialities of using the molecular Hartree-Fock model for reproducing the fractional HPS in the system of larger paramagnetic atoms and noble gas as illustrated by these present calculations on the LiHe and NaHe systems. In Sec. 2 we discuss the wave functions[8] for LiHe and NaHe; in Sec. 3 we give a summary of the fractional HPS calculation; we present the results in Sec. 4; and the conclusions in Sec. 5.

Table I. LiHe basis set.

N	L	Center	Orbital exponent
1	0	Li	4.590
1	0	Li	2.448
3	0	Li	1.048
2	0	Li	0.608
2	1	Li	2.854
2	1	Li	1.189
2	1	Li	0.512
3	2	Li	1.200
1	0	He	2.906
1	0	He	1.453
3	0	He	1.060
2	0	He	0.615
2	1	He	1.960
2	1	He	0.917
2	1	He	0.518
3	2	He	0.750

2. WAVE FUNCTIONS FOR THE LiHe AND NaHe

The MO-SCF wave functions[8] for LiHe and NaHe were computed using the BISON system.[9] The ground-state configuration for LiHe is $1\sigma^2 2\sigma^2 3\sigma^1$. The extended basis set for LiHe consists of 16 basis functions, four *s*, three *p*, and one *d* centered on the Li atom and a similar set centered on the He atom. The basis set, presented on Table I, was built up from the atomic set of Bagus and Gilbert,[10] an exhaustively optimized atomic set. For He, the accurate[10] set was used, while for Li, the nominal[10] set was employed. To this set were added polarization functions. The orbital exponents for the latter were optimized at 4 bohr. The set was then used to construct the wave functions at all other internuclear distances. For NaHe, the ground-state configuration is $1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma^2 5\sigma^1$. A total of 20 basis functions were used in constructing the wave function for NaHe. The basis set for He was carried over from the LiHe calculation. The set for Na, which consists of 12 basis functions (6*s*, 5*p*, and 1*d*), was formed from the nominal[10] set of Bagus-Gilbert to which polarization functions were added, and optimized at 4 bohr. See Table II.

3. FRACTIONAL HPS

The magnetic hyperfine interaction in paramagnetic atoms is fully stated in two terms, namely, the Fermi contact interaction[11]

$$H_F = 16\gamma_p \gamma_e \hbar^2 \textstyle\sum_i \vec{\mathrm{I}}_p \cdot \vec{\mathrm{S}}_i\, \delta(\vec{\mathrm{r}}_{pi}) \tag{1}$$

and the electron nuclear dipole-dipole interaction[12]

$$H_{dd} = \gamma_p \gamma_e \hbar^2 \sum_i \left(\frac{\vec{\mathrm{I}}_p \cdot \vec{\mathrm{S}}_i}{r_{pi}} - 3\, \frac{(\vec{\mathrm{I}}_p \cdot \vec{\mathrm{r}}_{pi})(\vec{\mathrm{S}}_i \circ \vec{\mathrm{r}}_{pi})}{r_{pi}{}^5} \right) . \tag{2}$$

Table II. NaHe basis set.

N	L	Center	Orbital exponent
1	0	Na	13.119
2	0	Na	11.259
3	0	Na	6.439
2	0	Na	3.040
3	0	Na	1.240
3	0	Na	0.750
2	1	Na	7.718
2	1	Na	4.171
2	1	Na	2.271
3	1	Na	0.8592
3	1	Na	0.5292
3	2	Na	1.904
1	0	He	2.906
1	0	He	1.453
3	0	He	1.060
2	0	He	0.615
2	1	He	1.960
2	1	He	0.917
2	1	He	0.518
3	2	He	0.750

$\gamma_e = e/2mc$ is the gyromagnetic ratio for the electron, γ_p is the gyromagnetic ratio for the nucleus of the paramagnetic atom P, $\vec{I}_p$ and $\vec{S}_i$ being, respectively, the spins of the nucleus of the paramagnetic atom and the ith electron with respect to the nucleus of atom P.

For paramagnetic atoms with spherical configuration, the contribution to the hyperfine interaction energy comes entirely through the Fermi contact term; while for atoms with nonspherical configurations, the contribution arising from the dipole-dipole term must be included. We will be dealing with paramagnetic atoms with spherical configurations. The magnetic hyperfine energy is obtained only from the Fermi contact term[11]

$$E_{\mathrm{hfs}} = (\psi | H_F | \psi) \;, \tag{3}$$

where ψ refers to the MOSCF function for the alkali–noble-gas system and finally takes the form

$$E_{\mathrm{hfs}}(R) = \tfrac{16}{3}\gamma_p \gamma_e a_0^{-3} \hbar^2 I_p \rho_p (r = r_p) \;, \tag{4}$$

where $\rho_p(r = r_p)$ is the electronic spin-density at the nucleus of the atom P (Li or Na, in our case) and R is the internuclear distance between the atom P and He.

Now, while interacting with He atoms, the alkali atom may instantaneously lose its spherical symmetry so that one may expect a second nonspherical contribution to the hyperfine energy. However, its statistical average (H_{dd}) over various relative positions of the He atom vanishes.

TABLE III. Spin density and integrand values for LiHe.

R (bohr)	Spin density[a] at Li nucleus (a.u.)	Integrand $\frac{\Delta_\nu(R)}{\nu_0} R^2 e^{-V(R)/kT}$ $(T = 387\,^\circ\mathrm{K})$
2	0.95733	0.0
3	1.26177	-1.0×10^{-6}
4	1.54548	-5.5×10^{-5}
5	1.67542	6.68×10^{-3}
6	1.68891	0.13362
7	1.67428	0.33518
8	1.66223	0.33414
9	1.65529	0.21423
10	1.65260	0.12519
12	1.65056	8.70×10^{-3}
15	1.65046	0.0

[a] Calculated from the open-shell orbital.

The dependence of the statistical ensemble average of the quantity

$$\frac{\Delta\nu(R)}{\nu_0} = \frac{E_{\mathrm{hfs}}(R) - E_{\mathrm{hfs}}(\infty)}{E_{\mathrm{hfs}}(\infty)} = \frac{\rho_p(R) - \rho_p(\infty)}{\rho_p(\infty)} \tag{5}$$

on the pressure of the rare gas is referred to as the fractional hyperfine pressure shift (HPS). Thus, the fractional HPS, the ensemble average of $\Delta\nu(R)/\nu_0$ for all the relative configurations of the alkali atom and He atom, is given by

$$f_p = \frac{\partial}{\partial p}\left\langle \frac{\Delta\nu(R)}{\nu_0} \right\rangle = \frac{4\pi a_0^3}{kT_0}\,\frac{10^6}{760} \times \int_0^\infty \frac{\Delta\nu(R)}{\nu_0}\, e^{-V(R)/kT} R^2 dR \tag{6}$$

in units of 10^{-9}/mm Hg, where k is the Boltzmann constant, a_0 the Bohr radius, T_0 is 273 °K, and T the absolute temperature of the experimental measurement. $V(R)$ is the interaction energy

$$V(R) = E(R) - E(\infty) \tag{7}$$

TABLE IV. Spin density and integrand values for NaHe.

R	Spin density[a] at Na nucleus (a.u.)	Integrand $\frac{\Delta_\nu(R)}{\nu_0} R^2 e^{-V(R)/kT}$ $(T = 295\,^\circ\mathrm{K})$
2	2.71491	0.0
3	3.95831	0.0
4	4.88855	-1.0×10^{-5}
5	5.33326	2.2×10^{-4}
6	5.42970	0.04808
7	5.40390	0.25118
8	5.36369	0.36396
9	5.33705	0.26757
10	5.32544	0.15327
12	5.31748	5.15×10^{-3}
20	5.31729	0.0

[a] Calculated from the open-shell orbital.

TABLE V. Fractional HPS for Li and Na in the He buffer gas.

Atom	Calculated values[a]	Experimental values
Li	78.87	77.7[b]
Na	78.11	73.0[b,c]

[a] In units of 10^{-9}/mm Hg.
[b] Reference 14.
[c] Reference 15.

for the alkali-helium system. The classical averaging, given by Eq. (6), is preferred to a quantum-mechanical averaging procedure, which would require knowledge of the motional wave function for the atom pair. Clarke[1] has shown that such a procedure only leads to a 3% improvement for the H-He system. Thus, from a knowledge of the change in electron spin density and the interaction energy, the hyperfine pressure shift may be calculated.

4. RESULTS AND DISCUSSION

The spin density at the alkali nucleus may be considered as a sum of two terms, a Hartree-Fock plus a correction due to electron correlation,

$$\rho_{\text{free atom}} = \rho_{\text{HF}} + \rho_{\text{corr}} \ . \tag{8}$$

The spin density of the alkali atom distorted by the helium atom may be considered in a similar manner,

$$\rho_{\substack{\text{distorted}\\ \text{atom}}} = \rho_{\text{HF,da}} + \rho_{\text{corr,da}} \ . \tag{9}$$

In order to evaluate the HPS we require the *change* in the spin density at the alkali nucleus rather than the *absolute* value of the spin density, the evaluation of which would require functions that go beyond the Hartree-Fock limit. Expressing the change in spin density in two terms, we have

$$\Delta\rho = \Delta\rho_{\text{HF}} + \Delta\rho_{\text{corr}} \ . \tag{10}$$

The OVC work on HHe[6] indicated that the correlation effect for that system was relatively small over quite a large range of separations.

For the change in Hartree-Fock spin-density calculation we have used the density due to the highest occupied orbital, the open-shell orbital of the alkali–noble-gas system. The interaction potential $V(R)$ used in these calculations was the one obtained from the extended-set calculations.[8] In these computations we have considered the internuclear separations of 15 and 20 bohr as the upper limit of integration in Eq. (6) and of Eq. (7) for LiHe and NaHe, respectively. The atoms pairs are well dissociated at these distances. We have considered that the electron spin densities at these limits would also represent those for two free alkali atoms. Very little error was made in making this approximation in the HHe calculation.[6]

The calculated value of the integrand in Eq. (6), as well as the spin densities calculated from the open-shell orbital, are presented in Tables III and IV for LiHe and NaHe. The integration indicated by Eq. (6) is done numerically. An exponential spline curve[13] was passed through the values of the integrand at the calculated points, then the integral of this curve is taken from a distance of 2 bohr to the infinity value assumed for the particular case, 15 for LiHe and 20 for NaHe.

Table V gives the calculated values of the fractional HPS f_p and the respective experimental values.[14, 15] The agreement between the calculated values and the experimental values of f_p is excellent in the LiHe case, and quite good in the case of NaHe.

5. CONCLUSION

While the evaluation of exact spin densities at the alkali nucleus requires a knowledge of the correlation effects,[16] the change in spin densities at the nucleus due to the approach of a noble-gas atom appears to be adequately represented by using wave functions of Hartree-Fock quality, and, as a corollary, the fractional hyperfine pressure shift can be successfully evaluated from a high-quality molecular-orbital SCF function.[17]

ACKNOWLEDGMENT

The authors are very grateful to Kurt Kaiser for use of his spline interpolation program.

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*Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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PHYSICAL REVIEW A VOLUME 2, NUMBER 6 DECEMBER 1970

Stark-Induced Quantum Beats in H LY$_\alpha$ Emission*

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(Received 6 April 1970; revised manuscript received 3 August 1970).

Intensity beats in the emission of Ly$_\alpha$ from beam-foil excited hydrogen in various static electromagnetic field configurations have been studied. The observed beat frequencies agree with the calculated values, which are independent of the field directions. The beat amplitudes, however, show significant dependence on the field directions relative to the beam. The theory for emission of light from the decay of coherently excited states is applied in the sudden perturbation limit. Agreement with experiment can only be obtained under the assumption that the foil excitation generates initial coherent wave functions $\Psi_{\mathrm{I,II}} = \alpha | p, \frac{1}{2}, \pm\frac{1}{2}\rangle + \beta | s, \frac{1}{2}, \mp\frac{1}{2}\rangle$, where $| l, j, m_j\rangle$ notation and the beam as quantization axis are used. The ratio α/β is then determined, which gives the ratio of the excitation cross section of the p to that of the s states as $\sigma_p/\sigma_s \geq 4 \pm 1$ at a beam energy of 200 (keV) per atom.

I. INTRODUCTION

Interference effects associated with the decays of coherently excited atomic states have been observed and studied for some time. Most of the interest has been concerned with decays after radiative or electronic excitation.[1] With the development of beam-foil spectroscopy,[2] a new excitation mechanism was introduced, which produces impulsive excitation as atoms pass through a thin foil in roughly 10^{-14} sec. In addition, it makes possible measurements with high time resolution. (In this experiment the excited atoms emerge from the foil with velocities of $\sim 5\times 10^8$ cm/sec, so that observation of 0.5 mm of beam length is equivalent to 10^{-10} sec.)

With this technique, periodic intensity fluctuations in exponential decays were observed when excited H or He$^+$ beams were exposed to static electromagnetic fields.[3] According to theoretical treatments of related phenomena,[4,5] this effect was interpreted as electric-field-induced interference between the decaying fine structure (fs) levels. From a more fundamental point of view, it is exactly the same as the aforementioned interference effects due to coherent excitations.[1] However, serious discrepancies between the observed and calulated frequencies were found.[3] Only recently was it pointed out, and shown with new measurements on some H Balmer lines,[6] that these discrepancies can be removed by interpreting the experimental intensity distribution as a superposition of several frequencies. These were obtained by considering all frequency differences between fs eigenvalues[7] of the same $|m_j|$ as possible oscillation frequencies. A frequency close to the theoretical one was also found in a recent experiment on H Ly$_\alpha$ emission.[8]

For further analysis of such experiments, however, it is necessary to know the amplitudes of these oscillations. That requires the calculation of the fs eigenfunctions in the applied field, which depend of course on the initially excited wave functions and on the directionally different field perturbations relative to the beam as the chosen quantization axis. This point has not been considered in the recent work[6,8] and has given rise to doubtful conclusions.

This paper makes use of the generalized treatment of multilevel coherence theory,[9] and shows experimental results which indicate the significance of different quantization axes in the clearest case of the mixing of $n = 2$ states in hydrogen.

II. THEORY

In order to describe an electric-field-induced quantum beat experiment using the beam-foil technique one has to distinguish between coherence introduced (a) by the excitation and (b) by the field. A separate description will be given for both cases,