III. CONCLUSION

Although the field dependence of the nuclear magnetic shielding for most substances should be unobservably small, there is the possibility that such a dependence could be observed for some substances in high-precision experiments in strong magnetic fields. The largest effects would be expected in molecules for which the chemical shifts of the magnetic shielding are abnormally large. As nuclear magnetic resonance experiments are made with greater accuracy and in higher magnetic fields, the proportionality of the resonance frequency to the magnetic field should not be automatically assumed, but should be experimentally verified.

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Birefringent Dispersion and the Nuclear Quadrupole Interaction

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This paper is an addendum to a paper by the author which presented a relation between the gradient of the electric field at the nucleus and dipole matrix elements. A scheme is suggested to take advantage of the result.

The gradient of the electronic electric field at the position of the atomic nucleus is required for an evaluation of nuclear quadrupole moments from the hyperfine *B* coefficients. Recently,[1] it was shown that this could be expressed by the sum rule

$$\langle 0|q|0\rangle = \frac{-m^2}{\hbar^4 N e^2} T(2)\ , \quad q = \sum_{i=1}^{n} \frac{P_2(\cos\theta_i)}{r_i^3}\ . \qquad (1)$$

N is the nuclear charge, n the number of electrons, m the electronic mass, and

$$T(j) = \sum_k (\epsilon_k - \epsilon_0)^{j+1} \times \left(\left|\langle 0| \sum_{i=1}^{n} z_i |k\rangle \right|^2 - \tfrac{1}{3} \left| \langle 0| \sum_{i=1}^{n} \vec{\mathrm{r}}_i |k\rangle \right|^2 \right)$$

or the equivalent in terms of dipole momentum or acceleration matrix elements. [We correct Eq. (7) of Ref. 1 by a factor of 2.] As we indicated in the earlier paper, the dipole matrix elements govern radiative transitions, so that $\langle 0|q|0\rangle$ may be deduced if measurements of rates are available. However, experimental techniques are insufficiently developed to apply Eq. (1) immediately. Our purpose in writing the present article is to point out how an approximate value of $T(2)$ may be extracted from a set of dispersion measurements.

The $T(j)$ are analogous in form to the scalar sum rules $S(j)$;

$$S(j) = \tfrac{2}{3} \sum (\epsilon_k - \epsilon_0)^{j+1} \left| \langle 0| \sum_{i=1}^{n} \vec{\mathrm{r}}_i |k\rangle \right|^2 \ .$$

Some well-known dipole sum rules for atoms are[2]

$$S(-2) = \bar{\alpha}/e^2, \quad \text{average static polarizability} \qquad (2)$$

$$S(-1) = \tfrac{2}{3} \langle 0| \left| \sum_{i=1}^{n} \vec{\mathrm{r}}_i \right|^2 |0\rangle \ , \qquad (3)$$

$$S(0) = n\, h^2/m \ , \quad f \text{ sum rule} \qquad (4)$$

$$S(2) = 4\pi N e^2 h^4 / 3m^2 \langle 0| \sum_{i=1}^{n} \delta(\vec{\mathrm{r}}_i) |0\rangle \ . \qquad (5)$$

Tensor sum rules are not restricted to $T(2)$. For example we have

$$T(-2) = \alpha'/3e^2, \quad \text{tensor static polarizability} \qquad (6)$$

$$T(-1) = \langle 0 | \left| \sum_{i=1}^{n} z_i \right|^2 - \tfrac{1}{3} \left| \sum_{i=1}^{n} \vec{\mathrm{r}}_i \right|^2 |0\rangle \ , \qquad (7)$$

$$T(0)=0\,,\quad \text{“depleted”}\ f \text{ sum rule}\ . \tag{8}$$

Dalgarno and his co-workers$^{3-6}$ have extensively applied the $S(j)$ to infer accurate values for the relevant atomic parameters. Their success suggests that similar schemes may be useful for properties associated with $T(j)$.

It may be shown^{5,6} that a variational calculation of the ac polarizability

$$\overline{\alpha}(\omega)=\tfrac{2}{3}e^2 \times\sum_k (\epsilon_k-\epsilon_0)\,|\langle 0|\sum_{i=1}^{n}\vec{\mathrm{r}}_i|0\rangle|^2/[(\epsilon_k-\epsilon_0)^2-(\hbar\omega)^2] \tag{9}$$

may be expressed as a *finite* summation

$$\overline{\alpha}(\omega)=\frac{2e^2}{3}\sum_{t=1}^{g}(\gamma_t-\epsilon_0)\,|\langle 0|\sum_{i=1}^{n}\vec{\mathrm{r}}_i|t\rangle \times[(\gamma_t-\epsilon_0)^2-(\hbar\omega)^2]^{-1}+O(\lambda_i^2)\ , \tag{10}$$

where the λ_i designate a set of (presumably small) variational parameters. The γ_t are poles of the variational trial function. Together with the squares of the effective matrix elements, they may be substituted into Eqs. (2–5) to estimate the $S(j)$. Chan and Dalgarno^5 applied these considerations to an analysis of the ground state of helium. They obtained excellent agreement with an accurate dispersion curve over a wide range of frequencies, and, for the most part, good values of $S(j)$ (see Table I). The correspondence is close in all cases except $S(2)$, the δ-function sum rule. We shall return to this discrepancy later and explain why a fractional error of comparable magnitude would not be expected in an estimate of $T(2)$ for a nonspherically symmetric system.

Chan and Dalgarno^5 perform a strictly theoretical variational calculation. This approach is not useful in many-electron systems, since the available approximate wave functions are much less accurate than those in heliumlike atoms. However, it is possible to analyze atoms and molecules of arbitrary complexity in terms of quantities obtainable from experiment alone.

Let $|\eta_J\rangle$, $J=1,\ g$ be a finite set of orthonormal functions. Assume that a unitary transformation is performed, reducing them to a set $|\xi_k\rangle$ in which the atomic Hamiltonian H_0 is diagonal, with matrix elements $H_{kk}=\langle\xi_k|H_0|\xi_k\rangle$. If a variational trial function of the form

$$|\psi_T\rangle=a_k|\xi_k\rangle$$

is constructed for calculating the ac polarizability, it follows that, with an error of second order,

$$a_k=\frac{2e(H_{kk}-\epsilon_0)\langle\xi_k|\sum_{i=1}^{n}\vec{\mathrm{r}}_i|0\rangle}{(H_{kk}-\epsilon_0)^2-(\hbar\omega)^2}\ ,$$

and

$$\overline{\alpha}(\omega)=e\sum_{k=1}^{g}a_k\langle 0|\sum_{i=1}^{n}\vec{\mathrm{r}}_i|\xi_\eta\rangle \equiv 2\sum\frac{(H_{kk}-\epsilon_0)M_k}{(H_{kk}-\epsilon_0)^2-(\hbar\omega)^2}\ . \tag{11}$$

We now show how the H_{kk} and the squares of the matrix elements may be deduced from measurable quantities alone. Let the original (nondiagonal) basis functions $|\eta_J\rangle$ be formally expanded according to $|\phi_L\rangle$, the true eigenfunctions of the system

$$|\eta_J\rangle=\sum C_{JL}|\phi_L\rangle\ .$$

The matrix elements of H_0 in the $|\eta_J\rangle$ representation are simply

$$H_{JI}=\sum_L C^*_{IL}C_{JL}\epsilon_L\,,$$

where the ϵ_L are the eigenenergies of the $|\phi_L\rangle$, presumably known spectroscopically. The free parameters C_{JL} are selected to ensure that the $|\eta_J\rangle$ form an orthonormal set and to include the relevant regions of Hilbert space. The computed H_{JI} are used to obtain the diagonal representation. The M_k may be deduced by fitting Eq. (11) to an experimental dispersion curve. As previously, these pseudomatrix elements and energies may be inserted into Eqs. (2–5) to calculate the $S(j)$.

Similar considerations apply to the $T(j)$, if one replaces the spherically averaged dispersion curve with a set of measured values of the ac tensor polarizability

$$\alpha'(\omega)=3e^2\times\sum_k\frac{(\epsilon_k-\epsilon_0)\,|\langle 0|\sum_{i=1}^{\eta}z_i|k\rangle|^2-\frac{1}{3}|\langle 0|\sum_{i=1}^{\eta}\vec{\mathrm{r}}_i|k\rangle|^2}{(\epsilon_k-\epsilon_0)^2-(\hbar\omega)^2}\ . \tag{12}$$

We return now to the question of the poor accuracy of $S(2)$ in helium and its relevance to an estimate of $T(2)$. Chan and Dalgarno^5 point out that $S(j)$ diverges logarithmically as $j\rightarrow 2.5$. $S(j)$ is understood to include an integral over the continuum, whose high-energy contribution assumes the form^7

TABLE I. $S(j)$ for ground state of He (Ref. 5).

j	Accurate values	Predicted values
-6	0.0323	0.0310
-4	0.0976	0.0950
-2	0.3478	0.3447
-1	0.7525	0.7523
0	2.00	2.00
$+1$	8.7	7.82
$+2$	121.3	53.3

$$S(j) \to \int_{\epsilon'}^{\infty} \epsilon_k^{j-7/2} d\epsilon_k \quad .$$

This indeed blows up as indicated. A large sampling of the continuum is indicated for $j \approx 2$.

A detailed examination of the asymptotic behavior of the matrix elements[7] reveals that, for electrons of arbitrary orbital angular momentum L, we have

$$S(j) \to \int_{\epsilon'}^{\infty} \epsilon_k^{j-7/2-L} d\epsilon_k \quad .$$

The singular behavior as $j \to 2.5$ arises solely from s electrons. Thus, if as is the case in the T-sum rules, only the bound p and higher L electrons contribute to the summation, the high-energy contribution to $T(j)$ is no worse than

$$T(j) \to \int_{\epsilon'}^{\infty} \epsilon_k^{j-9/2} d\epsilon_k \quad ,$$

which does not exhibit the divergence until $j \to 3.5$. (This obtains also in many-electron systems.) Consequently, it appears more appropriate to use the Chan-Dalgarno $S(1)$, not $S(2)$, as a model for $T(2)$.

To test this assertion, we calculated, by implicit summation,[8] $\alpha'(\omega)$ for the $2p$ state of atomic hydrogen at 80 wavelengths from the far infrared to the green. This is equivalent to an experiment. We obtain an accuracy of better than 1 part in 10^4 by expressing the solution to the characteristic inhomogeneous Schrödinger equation as a power series in the frequency. The coefficient of each term in the expansion may be calculated in closed form.[9] For $|\eta_J\rangle$, we made the simple choice of the |i.e. $|\eta_J$ hydrogenic states of $n=1$, $n=3$, and a linear combination of $n=4$ and $n=5$. We fitted by least squares a three-term summation for $\alpha'(\omega)$, using the expression

$$\alpha'(\omega) = \frac{3e^2}{(\hbar\omega)^2} \sum_k (\epsilon_k - \epsilon_0)^3 \times \left(\left| \langle 0 \right| \sum_{i=1}^{n} z_i \left| k \rangle \right|^2 - \tfrac{1}{3} \left| \langle 0 \right| \sum_{i=1}^{n} \vec{r}_i \left| k \rangle \right|^2 \right) \times \left[(\epsilon_k - \epsilon_0)^2 - (\hbar\omega)^2 \right]^{-1} \quad . \tag{13}$$

This formula is derived by recognizing that

$$\alpha'(\omega) = \frac{3e^2}{(\hbar\omega)^2} \sum (\epsilon_k - \epsilon_0) \times \left(\left| \langle 0 \sum_{i=1}^{n} z_i \left| k \rangle \right|^2 - \tfrac{1}{3} \left| \langle 0 \right| \sum_{i=1}^{n} \vec{r}_i \left| k \rangle \right|^2 \right) \times \left(-1 + \frac{(\epsilon_k - \epsilon_0)^2}{(\epsilon_k - \epsilon_0)^2 - (\hbar\omega)^2} \right) e \quad .$$

is identical to Eq. (12). Equation (13) follows from the depleted f sum rule. We guarantee in this manner that our set of matrix elements and energies satisfies Eq. (8).

TABLE II. Birefringent dispersion for $2p$ state of H. [$\langle 0 | q | 0 \rangle$ (fit) $= -0.007\,685\ a_0^{-3}$; $\langle 0 | q | 0 \rangle$ (exact) $= -0.008\,333\ a_0^{-3}$.]

Energy × 10^2 (units of 27.2 eV)	Tensor polarizability (a_0^3) Exact	Fitted
0.54	−30.17	−30.58
1.44	−31.26	−31.03
2.34	−33.59	−33.31
3.24	−37.76	−37.50
4.14	−45.26	−45.05
5.04	−60.43	−60.34
5.94	−103.17	−103.34
7.74	+95.00	+94.94
8.55	+29.95	+29.62

A synopsis of the comparison between exact and fitted values of $\alpha'(\omega)$ is shown in Table II. The fitted and exact $T(2)$ agree to within 8%, similar to the Chan-Dalgarno $S(1)$ and Sternheimer corrections.[10]

Experimental studies of birefringence in molecular gases via the Kerr effect have been made for many years.[11–13] (The ideas presented here apply to molecules as well as atoms.) With modern digitized data-taking techniques, it should be possible to achieve a level of accuracy both for absolute values of tensor polarizabilities and for the shape of dispersion curves sufficient to use the sum rules to advantage. Shearer[14] has recently optically pumped the metastable $^3P_2$ states of the rare gases, demonstrating that it is possible to orient nonspherical atoms. This presents a possible alternative to the Kerr effect for rendering gases optically anisotropic.

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$2p^2\ {}^3P$ and $2p3p\ {}^1P$ States of the Helium Isoelectronic Sequence*

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Accurate eigenvalues and radiative lifetimes are obtained for the bound $2p^{2}\,{}^3P$ and $2p3p\,{}^1P$ states of the heliumlike ions He I to Ne IX. A high-order Z-expansion perturbation procedure is used that does not require the explicit solution of perturbation equations. The results are compared with variational calculations. The predicted wavelengths of the $1s2p\,{}^3P$-$2p^{2}\,{}^3P$ and $1s3p\,{}^1P$-$2p3p\,{}^1P$ transitions in helium are, respectively, 320.31 and 308.97 Å. Lines have been observed in helium at 320.39 and 309.04 Å.

I. INTRODUCTION

Because of the conservation of angular momentum and parity, the $2p^{2}\,{}^3P$ and $2p3p\,{}^1P$ states of helium and heliumlike ions, although embedded in the continuum, are stable against autoionization within the *LS* coupling approximation. Their lifetimes depend on the probability of radiative transitions to lower states and are much longer than the lifetimes characteristic of autoionizing states. Becker and Dahler[1] have pointed out the importance of such highly energetic states as initiators of reactions involved in radiation chemistry and in the chemistry of high-temperature gases.

The $2p^{2}\,{}^3P$ state of helium has been produced through electron impact by Burrow and Schulz[2] and identified by the trapped-electron method. This state should also be observable in the electron energy-loss spectrum, although it has not yet been identified. The cross sections for the excitation of the $2p^{2}\,{}^3P$ and $2p3p\,{}^1P$ states by electron impact from the ground state have been calculated by Becker and Dahler,[1] along with several other doubly excited states. The $2p3p\,{}^1P$ state will be more difficult to observe in electron-impact experiments because its excitation cross section is much smaller than the $2p^{2}\,{}^3P$ cross section. A radiative transition at 320.39 Å, observed by Kruger[3] and included in Martin's[4] tables, has been tentatively identified as the $2p^{2}\,{}^3P$-$1s2p\,{}^3P$ transition.

The helium $2p^{2}\,{}^3P$ eigenvalue has been calculated by Holøien[5] using a configuration-interaction wave function. Several other less accurate calculations are cited by Becker and Dahler.[1] In this paper we report precise variational upper bounds for the $2p^{2}\,{}^3P$ and $2p3p\,{}^1P$ helium eigenvalues and oscillator strengths for radiative transitions to the $1s2p$, $1s3p$, and $1s4p\,{}^3P$ and ${}^1P$ states, respectively. The results are extended to the heliumlike ions by a high-order Z-expansion technique. We also calculate the sum of all oscillator strengths from the $1s2p\,{}^{1,3}P$ state to the $npn'p\,{}^{1,3}P$ states.

II. THEORY

The eigenvalue problem to be solved is (in Z^2 a.u.)

$$H\Psi_s = (H_0 + Z^{-1}V)\Psi_s = E_s\Psi_s\,, \tag{1}$$

where H_0 is a sum of two hydrogen-atom Hamiltonians, V is equal to $1/r_{12}$ and r_{12} and is the interelectronic coordinate. A variational approximation to E_s and Ψ_s is obtained from the stationary values