

Many-body study of van der Waals interaction involving lithium and rare-gas atoms and its contribution to hyperfine shifts

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Abstract. Using linked cluster many-body perturbation theory, the frequency-dependent dipole polarizabilities $\alpha(\omega)$ has been calculated for the lithium atom. The value of $\alpha(\omega)$ at the static limit ($169.04 a_0^3$) matches well with other available theoretical values and experimental results. These values have been used to calculate the van der Waals constants for interactions of lithium, helium and neon atoms. The values of the van der Waals constants for dipole-dipole interaction in atomic units are -22.9 , -44.8 , -1465.8 , 184950.0 , 2011.8 , 3896.5 , 30.3 , 59.0 and 115.1 for Li-He, Li-Ne, Li-Li, Li-Li-Li, Li-Li-He, Li-Li-Ne, Li-He-He, Li-He-Ne and Li-Ne-Ne interactions respectively. Obtaining the suitable response functions for lithium and helium atoms, the long range contribution to $\Delta a(r)/a_0$ in the study of fractional frequency shift in hyperfine pressure and temperature shift measurements is obtained as -541 atomic units.

Keywords. Many-body theory; lithium atom; hyperfine shift; dipole polarizability; van der Waals interaction.

1. Introduction

The long-range interaction between atoms has been analyzed successfully for a number of atoms by the linked cluster many-body perturbation theoretical (LCMBPT) procedure (Brueckner 1959; Kelly 1968). This method has been extensively used in studying the dynamic, polarizabilities of atoms (Dutta *et al* 1969b, 1970a) and, in addition, the van der Waals interaction energies between atoms (Dutta *et al* 1969a). It has also provided quantitative results for the influence of van der Waals interaction between atoms on the hyperfine pressure shift (Dutta *et al* 1970a, 1970b). In the present work we shall describe a LCMBPT investigation of lithium atom interacting with rare gas atoms, helium and neon.

Optical pumping experiments show that the hyperfine constant of the atom under study changes with the variation of the pressure and temperature of the buffer gas used in the bulb (Bernheim 1965). Theoretical explanations (Rao *et al* 1970) of this hyperfine pressure shift (HPS) and hyperfine temperature shift (HTS) show that these effects arise basically due to the short and long range interactions between the experimental atom and the buffer gas atoms. The long range contributions to HPS and HTS increase with the size of the buffer gas atoms. Also, the large polarizability of alkali atoms makes the effect of long range interactions on the hyperfine shifts even more important. In the past, attempts (Rao *et al* 1970; Ray *et al* 1968) to study the long range contributions to HPS using the variation-perturbation procedure have indicated

that this latter procedure has several disadvantages. These can be obviated if one uses the LCMBPT procedure involving frequency-dependent polarizability functions of the interacting atoms, specifically for imaginary frequencies. In the present work we have used the LCMBPT procedure to calculate the frequency-dependent dipole polarizabilities, $\alpha(\omega)$, and the HFS response functions for the lithium atom. Then using the available values of the $\alpha(\omega)$ of helium and neon atoms we have calculated the van der Waals energies for dipole interactions among Li, He and Ne atoms and the long-range contribution to the HFS and HFS for the lithium atom in the buffer gas medium of helium.

In § 2 the theoretical background is briefly presented. Section 3 deals with the numerical results and discussions.

2. Theory

The problem of studying interactions between atoms is usually complicated by the multicentre nature of the problem. However in the long-range region where the interaction is mainly due to the electrostatic multipole interactions, the problem can be reduced to a one-centre type (Margenau and Kestner 1969). For the study of the influence of interaction between the atoms on the hyperfine constant a we have to add two perturbing terms \mathcal{H}_{VDW} and \mathcal{H}_{hfs} to the zeroth order Hamiltonian \mathcal{H}_0 which itself is the sum of individual atomic Hamiltonians for atoms A and B .

$$\mathcal{H} = \mathcal{H}_A + \mathcal{H}_B + \mathcal{H}_{\text{VDW}} + \mathcal{H}_{\text{hfs}}, \quad (1)$$

where \mathcal{H}_{VDW} and \mathcal{H}_{hfs} are perturbations arising due to van der Waals interaction (between atoms A and B) and the Fermi contact interaction (for atom A) respectively. For \mathcal{H}_{VDW} we shall consider the dipole terms only, as the leading contribution arises from that. The lowest order in which the change in hyperfine energy occurs for interacting atoms is third order ($\Delta^3 E$) in \mathcal{H}' where \mathcal{H}' is the sum of the perturbing Hamiltonians, with two orders arising from \mathcal{H}_{VDW} and one from \mathcal{H}_{hfs} , leading to the expression

$$\Delta^3 E = \Delta^3 E_1 + \Delta^3 E_2 + \Delta^3 E_3,$$

where

$$\Delta^3 E_1 = \frac{12}{R^6} \sum_{i,j,k}^I \frac{\langle \psi_{0A} | Z_A | \psi_{iA} \rangle \langle \psi_{iA} | Z_A | \psi_{jA} \rangle \langle \psi_{jA} | \mathcal{H}_{\text{hfs}} | \psi_{0A} \rangle \langle \psi_{0B} | Z_B | \psi_{kB} \rangle^2}{(E_{oi}^A + E_{ok}^B) E_{oj}^A} \quad (2)$$

$$\Delta^3 E_2 = \frac{6}{R^6} \sum_{i,j,k}^I \frac{\langle \psi_{0A} | Z_A | \psi_{iA} \rangle \langle \psi_{iA} | \mathcal{H}_{\text{hfs}} | \psi_{jA} \rangle \langle \psi_{jA} | Z_A | \psi_{0A} \rangle \langle \psi_{0B} | Z_B | \psi_{kB} \rangle^2}{(E_{oi}^A + E_{ok}^B) (E_{oj}^A + E_{ok}^B)} \quad (3)$$

and
$$\Delta^3 E_3 = -\frac{6}{R^6} \langle \psi_{0A} | \mathcal{H}_{\text{hfs}} | \psi_{0A} \rangle \sum_{i,j}^l \frac{|\langle \psi_{oA} | Z_A | \psi_{iA} \rangle|^2 |\langle \psi_{oB} | Z_B | \psi_{jB} \rangle|^2}{(E_{oi}^A + E_{oj}^B)^2}$$
 (4)

Here R is the internuclear distance between atoms A and B . The suffices A and B correspond to individual atoms. The numerical suffices o, i, j and k correspond to the ground state of, i th, j th and k th excited states of the atoms, and

$$E_{oi}^A = E_o^A - E_i^A, \tag{5}$$

give the energy differences between the ground and excited atomic states. From a double perturbation theory the terms which are of magnitudes comparable with $\Delta^3 E_1$, $\Delta^3 E_2$, and $\Delta^3 E_3$ are given as

$$\begin{aligned} \Delta^3 E = & 2 \langle \delta\psi_{\text{VDW}} | \mathcal{H}_{\text{VDW}} | \delta\psi_{\text{hfs}} \rangle + \langle \delta\psi_{\text{VDW}} | \mathcal{H}_{\text{hfs}} | \delta\psi_{\text{VDW}} \rangle \\ & - \Delta E_{\text{hfs}} \langle \delta\psi_{\text{VDW}} | \delta\psi_{\text{VDW}} \rangle, \end{aligned} \tag{6}$$

and one can easily notice the equivalence of these terms with $\Delta^3 E_1$, $\Delta^3 E_2$ and $\Delta^3 E_3$ given above. Experimentally one usually measures the fractional shift which can be obtained by statistical averaging of the quantity given by

$$\frac{\Delta\alpha(R)}{a_0} = \frac{\Delta^3 E_1 + \Delta^3 E_2 + \Delta^3 E_3}{\langle \psi_{0A} | \mathcal{H}_{\text{hfs}} | \psi_{0A} \rangle} = \frac{1}{R^6} (D_1 + D_2 + D_3) = \frac{D}{R^6}. \tag{7}$$

For our purpose here we are interested only with the calculation of D_1 , D_2 and D_3 the use of which for HPS and HTS calculations have been presented in earlier work (Rao *et al* 1973).

Instead of using the perturbation Hamiltonian involving the interaction operator of the interacting atoms at long range as in expressions (2) through (6), we have used the convolution procedure involving the frequency dependent polarizabilities of the individual atoms to evaluate $\Delta^3 E_1$, $\Delta^3 E_2$ and $\Delta^3 E_3$ as well as the interaction energies $\Delta^3 E_4$ and $\Delta^3 E_5$ related to the van der Waals constants for two and three interacting atoms.

$$\Delta^3 E_1 = \frac{6}{\pi R^6} \int_0^\infty F_1^A(i\omega) a^B(i\omega) d\omega, \tag{8}$$

$$\Delta^3 E_2 = \frac{3}{2\pi^2 R^6} \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 F_2^A(i\omega_1, i\omega_2) \beta^B(i\omega_1, i\omega_2), \tag{9}$$

$$\Delta^3 E_3 = -\frac{3a_0}{2\pi^2 R^6} \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \beta^A(i\omega_1, i\omega_2) \beta^B(i\omega_1, i\omega_2), \tag{10}$$

$$\Delta^3 E_4 = -\frac{3}{\pi R^6} \int_0^\infty \alpha^A(i\omega) \alpha^B(i\omega) d\omega, \quad (11)$$

$$\Delta^3 E_5 = -\frac{3}{\pi R_{AB}^3 R_{BC}^3 R_{CA}^3} \int_0^\infty \alpha^A(i\omega) \alpha^B(i\omega) \alpha^C(i\omega) d\omega. \quad (12)$$

The response functions in (8) to (12) are defined by

$$F_1^A(\omega) = 2 \sum_{i,j}^l \frac{\langle \psi_{0A} | Z_A | \psi_{iA} \rangle \langle \psi_{iA} | Z_A | \psi_{jA} \rangle \langle \psi_{jA} | \mathcal{H}_{nfs} | \psi_{0A} \rangle E_{0i}^A}{[(E_{0i}^A)^2 - \omega^2] E_{0j}^A} \quad (13)$$

$$F_2^A(\omega_1, \omega_2) = 2 \sum_{i,j}^l \frac{\langle \psi_{0A} | Z_A | \psi_{iA} \rangle \langle \psi_{iA} | \mathcal{H}_{nfs} | \psi_{jA} \rangle \langle \psi_{jA} | Z_A | \psi_{0A} \rangle E_{0i}^A E_{0j}^A}{[(E_{0i}^A)^2 - \omega_1^2] [(E_{0j}^A)^2 - \omega_2^2]}, \quad (14)$$

$$\beta^A(\omega_1, \omega_2) = 4 \sum_i^l \frac{\langle \psi_{0A} | Z_A | \psi_{iA} \rangle \langle \psi_{iA} | Z_A | \psi_{0A} \rangle (E_{0i}^A)^2}{[(E_{0i}^A)^2 - \omega_1^2] [(E_{0i}^A)^2 - \omega_2^2]}, \quad (15)$$

and
$$\alpha^B(\omega) = 2 \sum_j^l \frac{\langle \psi_{0B} | Z_B | \psi_{jB} \rangle \langle \psi_{jB} | Z_B | \psi_{0B} \rangle E_{0j}^B}{(E_{0j}^B)^2 - \omega^2}. \quad (16)$$

The response $\alpha^B(\omega)$ of course corresponds to the frequency-dependent polarizability for the atom B .

At this point the requirement is to obtain the atomic wave functions perturbed by a time-dependent external field. As usual in the time-dependent LCMBPT (Dutta *et al* 1969) for an atom A

$$\mathcal{H}_A = \mathcal{H}_{0A} + \mathcal{H}_{1A} + \mathcal{H}'_A(t), \quad (17)$$

whence
$$\mathcal{H}_{0A} = \sum_{i=1}^N \left(-\frac{1}{2} \nabla_i^2 - \frac{N}{r_i} + V_i \right),$$

$$\mathcal{H}_{1A} = \sum_{i < j} \frac{1}{r_{ij}} - \sum_i V_i,$$

and
$$\mathcal{H}'_A(t) = \sum_{i=1}^N [\mathcal{E}_0 Z_i \exp(i\omega t) + \text{c.c.}], \quad (18)$$

Here N is the number of electrons in atom A . As the ground state wave functions ψ_{oA} are not known exactly one has to start with the zeroth order wave function φ_{oA} which is an eigen-function of \mathcal{H}_{oA} . The difference between the actual Hamiltonian H_A and \mathcal{H}_{oA} has to be handled as a perturbation \mathcal{H}_{1A} in addition to the extra perturbation $H'_A(t)$ arising from the external electric field. For each atom, this type of double perturbation formalism is used in the LCMBPT framework. In general we shall drop the atomic suffix A and will treat each atom individually. Following the double perturbation theory we shall have to study the effects of H_1 and $H'(t)$ upto various orders in each. Then one can obtain the complete expansion of each wave-function $\psi(t)$ in terms of various effects and one can sum them up to different orders depending upon the accuracy needed. These constituent wave functions can be expressed as Feynman diagrams for ease in representation and handling. Then the response functions can also be represented by sums of various diagrams. In drawing these diagrams and their permutations the usual rules (Chang *et al* 1968) for the signs and linking are to be followed. Since the techniques for evaluation of the diagrams involving complete sets of H_{oA} and H_{oB} are described extensively earlier (Dutta *et al* 1970) for the response functions in hydrogen, helium and neon atoms and since the basic analysis of many-body diagrams for atomic properties have also been well documented, we shall not repeat them here. At one or more instances in the next section dealing with results we shall, however, present expressions for a few diagrams for completeness.

In the study of the HPS and HTS of lithium atoms in helium or neon buffer gases, lithium atom was considered to be the atom A . Dependent on the buffer gas, helium or neon was considered to be atom B . In the present calculations the complete set of bound and continuum single particle states for the ground state $2s$ of lithium were computed by numerically solving the one-electron equation in the usual way using the V^{N-1} potential (Chang *et al* 1968) in the place of V_i in (18). The occupied state ($1s$ and $2s$) energy and the wave functions agreed with available Hartree Fock values (Clementi 1965) upto five significant figures. As expected, the $1s$ hole state energy differed from the Hartree-Fock results slightly due to the V^{N-1} potential used. This difference was corrected by the usual ladder diagrams. Using these wave functions, different single and double excitation matrix elements were calculated and stored to be used later to compute the response functions.

3. Results and discussion

We discuss first the simplest of the response function in (13) through (16), namely, $a(\omega)$ for lithium atom. All possible diagrams were drawn using the expression (16) and LCMBPT expansion for ψ_{oB} and ψ_{jB} . As is obvious from the definition of \mathcal{H}_{1A} in (18) this introduces electron correlation in the wave functions of atom A . In general, for any atom, the effect of various orders of \mathcal{H}_1 have to be considered. Therefore depending upon the orders of correlation (\mathcal{H}_1) involved $a(\omega)$ was rewritten as

$$a(\omega) = a_0(\omega) + a_1(\omega) + a_2(\omega) + \dots \quad (19)$$

Only two diagrams occurred for $\alpha_0(\omega)$ which are given in figure 1. In the next order contribution $\alpha_1(\omega)$ many diagrams are possible. On drawing all distinct diagrams following the usual recipe to expand the corrections due to the V^{N-1} potential and going through mutual cancellations finally 15 diagrams were obtained for $\alpha_1(\omega)$. Out of these only the topographically distinct ones have been presented in figure 2. In presenting these we have left out diagrams which are indistinguishable from each other except in the labelling of the internal lines. We have also followed the "Brandow" convention (Brandow 1967) where only the direct diagrams are drawn and the exchanges are suppressed. In these the diagrams of the type 2(e) and their exchange counterparts represent the first order correction to the polarizability due to the self-consistent interaction between the perturbed hole states. Figures of the type 2(d) and their rearrangements represent two particle correlation. While evaluating diagrams of figures 1(a) and 1(b) it was observed that the diagrams involving $2s \rightarrow 2p$ excitations contributed substantially larger values to $\alpha_0(\omega)$ than the others as was also the case for the static polarizability for lithium. This is a consequence of the small gap between the $2s$ and $2p$ states in the case of lithium and the strong overlap between the $2s$ and $2p$ states leading to large matrix element for Z . As a result, among the diagrams in figure 2, only the diagrams that involved the perturbation of $2s$ hole states were found to make significant contributions to $\alpha_1(\omega)$. Typical expressions for the diagrams for the dynamic polarizability $\alpha_0(\omega)$ and $\alpha_1(\omega)$ are given below.

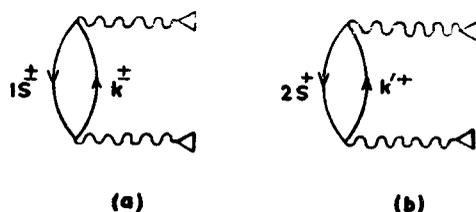


Figure 1. Diagrams for $\alpha_0(\omega)$

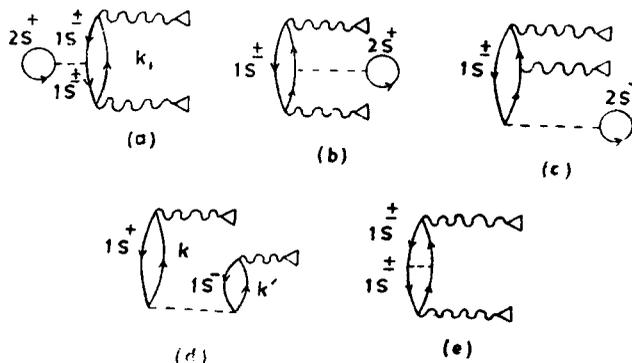


Figure 2. Diagrams for $\alpha_1(\omega)$

For figures 1(a) and 1(b)

$$a_0(\omega) = - \sum_{m, k} |\langle m | Z | k \rangle|^2 \frac{2 \epsilon_{mk}}{\epsilon_{mk}^2 - \omega^2}, \quad (20)$$

and for figure 2(d)

$$a_1(\omega) = \sum_{\substack{mm' \\ kk'}} \langle m | Z | k \rangle \langle k' k | \frac{1}{r_{12}} | m' m \rangle \frac{2 \epsilon_{mk} \langle m' | Z | k' \rangle}{(\epsilon_{mk} + \epsilon_{m'k'}) (\epsilon_{mk}^2 - \omega^2)}. \quad (21)$$

The summations over m and m' are taken over the hole states, *i.e.*, occupied $1s$ and $2s$ states from which excitations occur to unoccupied or particle states. Possible m states are indicated in figure 1. ϵ_{mk} has a meaning similar to E_{0i} in (5), namely the energy difference $\epsilon_m - \epsilon_k$ between hole state m and particle state k .

Before presenting our results for $a(\omega)$ we would like to point out the accuracy of the wave functions used in our LCMBPT procedure. These have been obtained by solving the one-electron type Schrödinger equation for \mathcal{H}_0 . On calculations of the resultant excitation energies we have obtained good agreement with spectroscopic data. This indicates the success of the numerical procedure used. This is important because we shall use these basis states for calculating the long range effects on the hyperfine interaction and three-body van der Waals interaction energies. For the static polarizability $a(0)$ we have used the contributions from all the possible diagrams of the $a_0(0)$ and $a_1(0)$ type. We have also included the effects of selected second order diagrams (shown in figure 3) which make major contribution to $a_2(0)$. In table 1 we have compared the contributions to $\alpha_0(0)$ from various excitations. In table 2 the values of different diagrams are given. Our final result for $a(0)$ is $169.04 a_0^3$ which is in good agreement with the most recent experimental result (Molof *et al* 1974) of $(164 \pm 3) a_0^3$. Our $a(0)$ value also compares well with recently calculated values (Lamm and Szabo 1980) of $164 a_0^3$ to $171.5 a_0^3$.

We consider next our result for $a(\omega)$, which is related to the refractive index $n(\omega)$ by the Lorentz-Lorentz law. For comparison with experiment, it is helpful to consider the function $[n^2(\omega) - 1]$, the result of which at various ω from our calculations

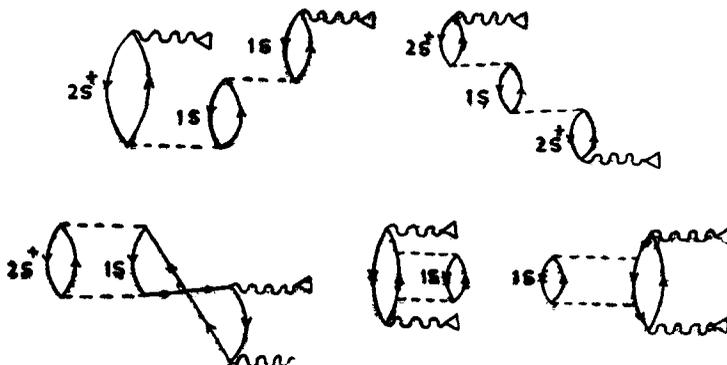


Figure 3. Some diagrams for $a_2(\omega)$. Only these were included in the calculation along with all possible permutations and rearrangements.

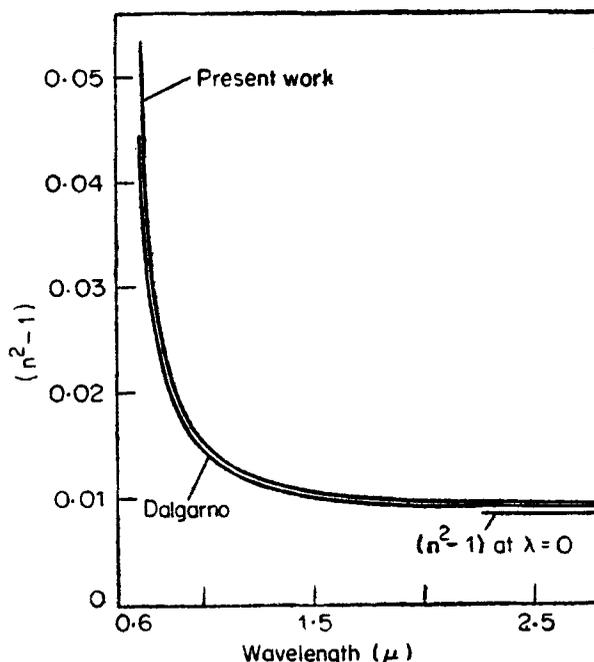


Figure 4. Dependence of $(n^2 - 1)$ on the wavelength. Asymptotic value for the present work is indicated in the plot.

are plotted in figure 4. In the same figure the plot from a calculation (Stacey and Dalgarno 1968) by a different procedure is also given. Also the values of their static polarizability $\alpha(0)$ $163.195 a_0^3$ and $(n^2 - 1)$ at zero frequency limit of 0.008187 are to be compared with our $\alpha(0)$ and $(n^2 - 1)$ at zero frequency limit, $169.04 a_0^3$ and 0.008484 respectively. It is interesting to note that both the $[n^2(\omega) - 1]$ curve from earlier work and the corresponding results for $\alpha(0)$ and $[n^2(0) - 1]$, while in fairly good agreement with our results, appear to be smaller in magnitude than our results in all cases. There are no experimental results for $[n^2(0) - 1]$ to compare with the plots on figure 4. Out of the many types of calculations for $\alpha(\omega)$ that exist two have been used widely. The time-dependent variation perturbation method (Karplus and Kolker 1964) and the time-dependent Hartree Fock theory (Stewart 1975) have yielded the values for $\alpha(\omega)$ for many atoms and ionic sequences. We shall compare the results of these theories with that of the LCMBPT later.

Continuing the calculation of the van der Waals interaction energy between lithium and the rare gas atoms helium and neon, as well as another lithium atom we have carried this out using equation (11) and obtained the corresponding dipolar van der Waals constants C_{AB} (in the van der Waals energy expression C_{AB}/R^6). Similarly we have also derived the van der Waals constants C_{ABC} for three-atom interacting system involving lithium, helium and neon atoms using (12).

For obtaining the $\alpha(i\omega)$ occurring in equations (11) and (12) for any atom one has to follow the procedure described for $\alpha(\omega)$ but with ω replaced by $i\omega$ during the evaluation. Thus, in (20) and (21), the $-\omega^2$ terms in the denominator were replaced by $+\omega^2$. For lithium, a set of $\alpha(i\omega)$ for different ω to be used in (11) and (12) were obtained as for $\alpha(\omega)$ by evaluating the diagrams in figures 1 through 3. For $\alpha(i\omega)$ of

helium and neon, the values are available from earlier work (Dutta *et al* 1969b, 1970a) and these were used in obtaining C_{AB} and C_{ABC} from (11) and (12), involving the pair and triple interactions among lithium, helium and neon atoms, A referring always to lithium atom. The values obtained for the binary interaction constants C_{AB} are presented in table 3. In this table the results from the use of only $\alpha_0(i\omega)$ and those from the use of full $\alpha(i\omega)$ are compared. These results show that the effects of the electron-electron interactions represented by the influence of $\alpha_1(i\omega)$ and $\alpha_2(i\omega)$ on $\alpha(i\omega)$ in equation (11) are relatively small but not insignificant. In table 4 the results for three-atom interactions are presented using our net calculated $\alpha(i\omega)$ for lithium and the results for $\alpha(i\omega)$ for helium and neon from earlier work. For comparison, the available values of C_2^{AB} and C_2^{ABC} from earlier variational work and recent work

Table 1. Contributions to $\alpha_0(\omega)$ in atomic units for lithium atom from $m \rightarrow k$ excitations at $\omega = 0$.

Values of particle state k	$m = 1s$	$m = 2s$
2p	0.01578	167.27610
3p	0.00464	0.17325
4p	0.00193	0.12894
5p	0.00098	0.09636
6p	0.00056	0.04011
7p	0.00035	0.02690
8p	0.00024	0.01784
9p	0.00017	0.01158
10p	0.00012	0.00866
Continuum	0.13270	1.17801

Table 2. Contributions to $\alpha(\omega = 0)$ in atomic units from different diagrams.

Figure	Contribution
1(a)	0.15748
1(b)	168.03074
2(d)	-0.00252
Counterpart of figure 2(d) with $2s^+$ hole	-0.26905
Exchange counterpart of figure 2(d)	0.02772

Table 3. The van der Waals constants for interaction of lithium atom with helium and neon in atomic units.

System	C_2^{AB}		C_2^{AB} (Stacey 1968)	C_2^{AB} (Lamm and Szabo 1980)
	Lowest order diagrams	Total		
Li-He	-24.49	-22.88	-22.49	-22.0
Li-Ne	-44.97	-44.83		-42.8
Li-Li	-1470.83	-1465.81	-1391.00	-1380

Table 4. The van der Waals constants for three-body interactions.

System	C_2^{ABC} (Atomic units) from this work	C_2^{ABC} (Atomic units) (Dalgarno 1967)	C_2^{ABC} (Atomic units) (Lamm and Szabo 1980)
Li-Li-Li	184950.00	169000.9	170000.9
Li-Li-He	2011.78	1910.0	
Li-Li-Ne	3896.46		
Li-He-He	30.29	29.60	
Li-He-Ne	59.02		
Li-Ne-Ne	115.08		

by asymptotic procedures are also listed in tables 3 and 4. In the variational work, a variational configuration interaction approach was utilized. Our results for all the quantities $[n^2(\omega) - 1]$, C_2^{AB} and C_2^{ABC} from figure 4 and tables 3 and 4 respectively appear to agree very well overall with the results of other investigators for these quantities where the latter are available. It appears, however, that the variational results, which also include many-body effects through configuration interaction, are consistently somewhat smaller than our results. A possible reason for this trend could be that the configuration interaction approach does not involve all the excited configuration spanned by the many-body perturbation diagrams in figures 1, 2 and 3. For a final comparison one can look at the values of C_2^{AB} available from the time-dependent Hartree-Fock calculations (Stewart 1975) which yield a value of 1480 against our value of 1465.9. The value of C_2^{ABC} for lithium atom given by the same approach is 188000 while our value is 184950. All these are within comparable range.

Finally, we shall discuss our results for the response functions $F_1^A(i\omega)$ and $F_2^A(i\omega)$ in equations (13) and (14) that occur in expressions (8) and (9) for the energy terms related to the hyperfine shift. Considering first $F_1^A(i\omega)$, the diagrams involving zero order and first order effects of electron-electron interaction are presented in figure 5. In these diagrams the hyperfine vertices have been represented by wiggly lines ending in a large dot. Since the hyperfine operator involves a δ -function, in these diagrams one must connect the hyperfine vertex to *S* states only. The + and - superfaces noted on the lines representing electronic states refer to up and down spins respectively. There are, of course, algebraic cancellations between + and - states wherever they can both occur. As in works on hyperfine interactions in isolated atoms, we have applied these cancellations before evaluating the diagrams to avoid having to handle differences of large numbers and consequent lower accuracy. The contributions from the various diagrams in figure 5 are tabulated in table 5, the largest contribution seemingly arising from figure 5(b) where the valence 2^+ state is the hole state connected to the hyperfine and external field vertices. One also must notice that among the rest of the diagrams the most important contribution arises from the diagram in figure 5(g). This diagram represents the exchange core polarization contribution to the hyperfine constant which is known to be rather important, about 30% of the direct contribution in the isolated atom. In the present case where the effects of the external field vertices are included, it is only about 5% of the direct contribution from the direct diagrams 5(a) and 5(b) and opposite in sign. In view of this feature of substantially reduced relative importance of exchange core polarization for the hyperfine shift as compared to that in the case of the hyperfine inter-

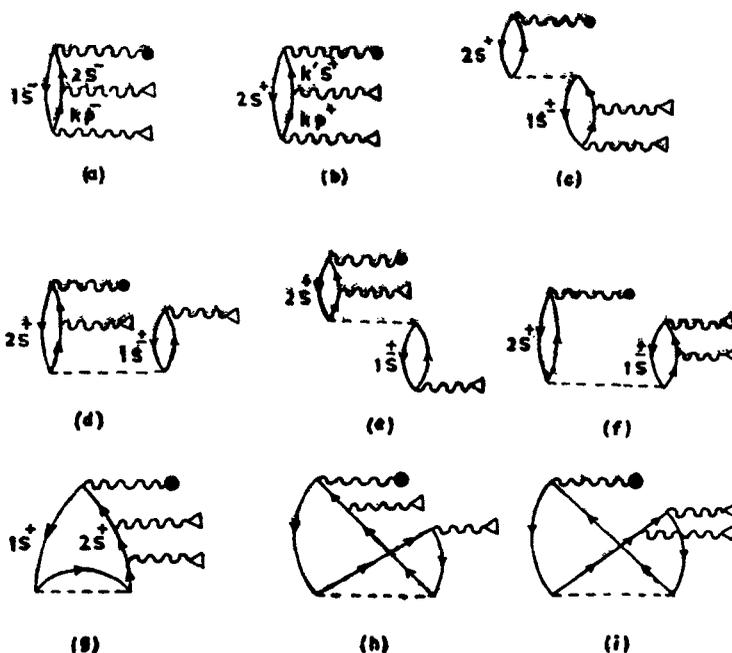


Figure 5. Some diagrams for $F_1^A(\omega)$.

Table 5. Contribution to $F_1^A(i\omega)$ for lithium atom from various diagrams at $\omega = 0$.

Figure	Contribution (Atomic units)
5(a)	0.03833
5(b)	-195.44136
5(c)	0.12635
5(d)	-0.35676
5(e)	-0.35676
5(f)	0.12635
5(g)	10.34433
5(h)	1.07464
5(i)	-0.99791

action of the isolated atom, it appears reasonable to conclude that correlation effects on the hyperfine shift involving two orders in $1/r_{12}$ will be relatively small in effect. Thus in the isolated lithium atom, correlation effects contribute only about 7% of the direct contribution. On reducing this effect by the same factor of about six as in the case of the exchange core polarization contribution to the hyperfine shift, one expects only about 1% of the direct contribution. In view of this, we have not carried out an explicit evaluation of the correlation diagrams, which would have required substantial additional effort.

The response functions $\beta(\omega_1, \omega_2)$ for both the interacting atoms can be easily evaluated using the diagrams similar to those used for $\alpha(\omega)$. As can be observed

from (14) and (16) the only difference between $\alpha(\omega)$ and $\beta(\omega_1, \omega_2)$ arises from the energy denominators. These have been drawn in figure 6 and can be compared to the diagrams in figures 1 through figure 5. Of the four important diagrams shown in figure 6, only the two lowest order diagrams and consistency diagrams were evaluated.

Examination of equations (3) and (6) shows that $\Delta^3 E_2$ is of the form $\langle \delta\psi_{VDW} | \mathcal{H}_{hfs} | \delta\psi_{VDW} \rangle$. The perturbation due to van der Waals interaction mixes non- s -like character and therefore, this term vanishes due to the δ -function property of the Fermi-contact operator. Hence, in the variation-perturbation work, this term was left out. However, a study of (9) and (14) reveals that when two orders of $(1/r_{12})$ interaction are included, one can draw non-vanishing diagrams for $F_2^A(\omega_1, \omega_2)$ which would give non-zero contribution to $\Delta^3 E_2$. A few such diagrams are drawn in figure 7.

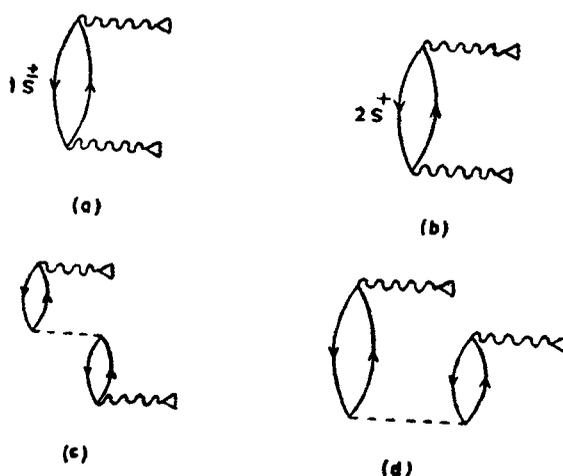


Figure 6. Some diagrams for $\beta^A(\omega_1, \omega_2)$.

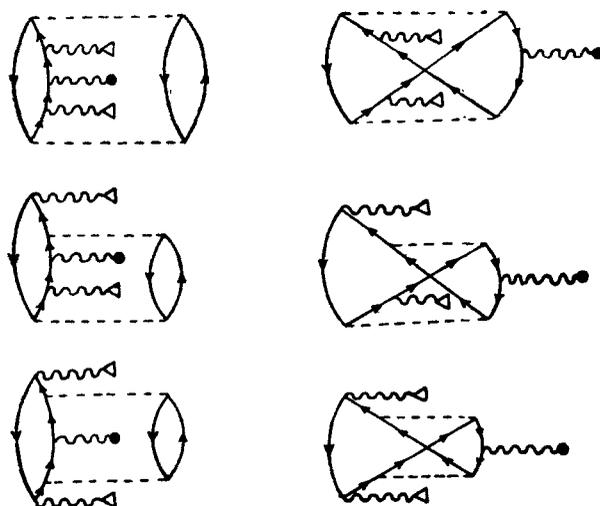


Figure 7. Lowest order diagrams for $F_2^A(\omega_1, \omega_2)$.

Table 6. Values of D_1 and D_3 for the HPS of the Li-He system in atomic units.

	D_1	D_3	$D = D_1 + D_3$
Lower order diagrams	-780.27	-23.09	-803.36
Final values including consistency and correlation	-519.51	-21.73	-541.23

This contribution to $\Delta^3 E_2$ thus has a purely many-body origin. Since the lowest possible F_2^A diagrams are of the second order in $1/r_{12}$, their contributions and hence $\Delta^3 E_2$ were found to be negligible.

After evaluating the response functions $F_1^A(i\omega)$, $F_2^A(i\omega_1, i\omega_2)$ and $\beta^A(i\omega_1, i\omega_2)$ (A referring to lithium) and using $\alpha^B(i\omega)$ and $\beta^B(i\omega_1, i\omega_2)$ (with $B =$ helium or neon from earlier work) the integrations were performed according to (8), (9) and (10) to obtain $\Delta^3 E_1$, $\Delta^3 E_2$ and $\Delta^3 E_3$. The second quantity, $\Delta^3 E_2$, was of course negligible as remarked earlier and so was D_2 related to it by (7). The D_1 and D_3 values related to $\Delta^3 E_1$ and $\Delta^3 E_3$ in (7) are listed in table 6. In both cases, the values obtained from only the lowest order diagrams without the effects of intra-atomic electron-electron interactions and then the final values including the influence of these interactions are presented. The net long range shift in the hyperfine interactions is thus given by $-541/R^6$, with a confidence limit of about 1% from the combined effects of both higher order diagrams not considered in figures 5, 6, and 7 and the limits of our computational accuracy. It is important to note from table 6 that the consistency and correlation effects produce a contribution of more than 30% in magnitude and an opposite sign as compared to the zero-order contribution to D , a feature similar in nature to the contributions from electron-electron interaction effects to the hyperfine constant of isolated lithium atom.

In summary, we have presented results of a LCMBPT study of lithium atoms interacting with helium and neon atoms at a long range. Accurate frequency-dependent polarizabilities for lithium and van der Waals constants for different interactions have been given including many-body effects. These values have been compared with some well-known available theoretical results and, in the case of static polarizability of lithium, with a recent experimental value. Thus these results should be acceptable as standard and can be compared with the results from any good technique (for example see the review of many techniques in the article of Oddershede 1978). The contribution of long-range interaction of lithium with buffer helium gas represented by the term D/R^6 for HPS and HTS experiments is calculated. This value of D combined with short range effects (Rao *et al* 1973) is needed for the understanding of HPS and HTS in optical pumping experiments on lithium. It is hoped that results for D will be available by other procedures in future for comparison with the present values, and to test the conclusion regarding the significant importance of electron-electron interaction effects.

References

- Bernheim R A 1965 *Optical pumping* (New York: Benjamin)
 Brandow B 1967 *Rev. Mod. Phys.* **39** 771

- Brueckner K A 1959 *The many-body problem* (New York: John Wiley)
- Chang E S, Pu R T and Das T P 1968 *Phys. Rev.* **174** 1
- Clementi E 1965 *Tables of atomic functions* (San Jose: IBM)
- Dalgarno A 1967 *Adv. Chem. Phys.* **12** 143
- Dutta N C, Ishihara T, Matsubara C and Das T P 1969a *Int. J. Quant. Chem.* **3S** 8
- Dutta N C, Ishihara T, Matsubara C and Das T P 1969b *Phys. Rev. Lett.* **22** 8
- Dutta C M, Dutta N C, Ishihara T and Das T P 1970a *Phys. Rev.* **A1** 561
- Dutta C M, Dutta N C and Das T P 1970b *Phys. Rev.* **A2** 30
- Karplus M and Kolker H 1964 *J. Chem. Phys.* **41** 3955
- Kelly H P 1968 *Adv. Theor. Phys.* **2** 196.
- Lamm G and Szabo A 1980 *J. Chem. Phys.* **72** 3354
- Margenau H and Kestner N R 1969 *Theory of intermolecular forces* (New York: Pergamon)
- Molof R W, Schwartz H L, Miller T M and Bederson B 1974 *Phys. Rev.* **A10** 1131
- Oddershede J 1978 *Adv. Quant. Chem.* **11** 275
- Rao B K, Ikenberry D and Das T P 1970 *Phys. Rev.* **A2** 1411
- Rao B K, Ikenberry D and Das T P 1973 *Phys. Rev.* **A8** 1673
- Ray S, Lyons J D and Das T P 1968 *Phys. Rev.* **174** 104
- Stacey G M and Dalgarno A 1968 *J. Chem. Phys.* **48** 2515
- Stewart R F 1975 *J. Phys.* **B8** 1