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Many-Body Approach to the Hyperfine Pressure Shift in Optical-Pumping Experiments*

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The formulation of the van der Waals (VDW) interaction between atoms in terms of frequency-dependent polarizabilities is extended to the problem of the long-range contribution to the hyperfine pressure shift in optical-pumping experiments. The requisite perturbed-energy expression for the present problem involves two orders of VDW interaction and one order of magnetic hyperfine interaction. This expression is recast in terms of integrals involving requisite frequency-dependent response functions which are evaluated using the Brueckner-Goldstone many-body technique applied earlier to VDW energy calculations. Specific applications are made to H-He and H-Ne systems. The fractional shift $\Delta\mathcal{A}/\mathcal{A}_0$ of the hyperfine constant is expressed in the form of D_{HX}/R^6, where R (a.u.) is the separation between H and X atoms. The values we obtain for D_{HX} are 13.34 and 26.13 for X= He and Ne, respectively. This analysis removes one of the important uncertainties in hyperfine-pressure-shift calculations, namely, the influence of correlation effects on the long-range part of $\Delta\mathcal{A}/\mathcal{A}_0$.

I. INTRODUCTION

The Brueckner-Goldstone (BG) many-body perturbation theory has recently been adapted to the problem of interatomic forces.[1] The formulation of the procedure utilized an expression for the van der Waals (VDW) energy of the interacting atoms in terms of the frequency-dependent polarizabilities, $\alpha(\omega)$ for the individual atoms,[2] and BG theory was applied specifically to the calculation of $\alpha(\omega)$. It is, however, straightforward to extend the BG procedure to other properties of interacting atoms besides the VDW energy, the only difference being that one then has to handle other response functions besides $\alpha(\omega)$. In particular, as pointed out in earlier work,[1,3] it is desirable to extend the BG theory to the study of hyperfine pressure shifts (HPS) of atoms with unpaired spins (referred to hereafter as paramagnetic atoms) in buffer-gas atmospheres. Our present work is addressed to the problem of calculating the long-range contribution to HPS through the use of many-body theory. The long-range contribution to HPS of paramagnetic atoms has been evaluated in the past through the use of variation-perturbation techniques.[4] Results obtained by this latter technique have the usual disadvantage of being sensitive to the form of the variation function chosen. The BG procedure, in addition to removing this uncertainty, has three other advantages. First, it allows us to include conveniently the influence of intraatomic correlation effects. Second, for the heavier buffer-gas atoms which are more polarizable, the long-range effect is of major importance and an accurate procedure for its calculation is desirable for comparison with experiments. Finally, in the case of smaller buffer-gas atoms, where short-(and intermediate-) range interactions are of importance, one can derive the "experimental" values of such contributions to HPS by subtracting the accurately calculated value of the long-range contribution from the experimental HPS. These derived, experimental values of the short-range HPS could then serve as references for assessing the accuracy of theoretical procedures developed for their evaluation. At the present time, short-range effects are included only partially through orthogonalization techniques that incorporate the influence of Pauli correlation of electronic orbitals of the interacting atoms. Although the present paper deals with the specific cases of hydrogen-helium and hydrogen-neon systems, the procedure developed is quite general and should be easily applicable to more complicated paramagnetic atoms with a number of core states and more than one valence electron outside the closed shell.

In Sec. II we present the essential features of the BG theory as applied to the HPS problem. Prescriptions are obtained for deriving the requisite response functions through the diagrammatic techniques of many-body perturbation theory. In Sec. III we present results of our calculation on H-He and H-Ne systems and discuss their significance.

For the sake of simplicity, we shall assume the atoms are spherical, which is adequate for the specific systems to be studied here. The procedure developed here can, however, be easily extended to nonspherical atoms.

II. FORMULATION OF FREQUENCY SHIFT IN TERMS OF FREQUENCY-DEPENDENT RESPONSE FUNCTIONS

In developing the theory for HPS, we start with the paramagnetic atom A located at a distance R from the inert-gas atom B, the latter being in its ground state. The internuclear distance R is assumed to be large enough so that the charge clouds associated with the individual atoms do not overlap significantly. In the absence of interatomic interactions, the atoms A and B are described by their respective nonrelativistic atomic Hamiltonians $\mathcal{H}^A$ and $\mathcal{H}^B$ with corresponding eigenfunctions Ψ_{iA} and Ψ_{jB} and eigenvalues E^A_i and E^B_j, respectively. Then the zero-order approximation to the problem is described by the Hamiltonian $\mathcal{H}_0$:

$$\mathcal{H}_0 = \mathcal{H}^A + \mathcal{H}^B \quad , \tag{1}$$

with eigenvalues $E_{ij} = E^A_i + E^B_j$,

and eigenfunctions

$$\Psi_{ij} = \Psi_{iA}\Psi_{jB} \quad . \tag{2}$$

To study the influence of the interaction between the atoms on the hyperfine constant $\mathcal{A}$, we have to add two perturbing terms $\mathcal{H}_{\rm VDW}$ and $\mathcal{H}_{\rm hfs}$ to $\mathcal{H}_0$, leading to the total Hamiltonian $\mathcal{H}$:

$$\mathcal{H} = \mathcal{H}_0 + \mathcal{H}' \quad , \tag{3}$$

with $\mathcal{H}' = \mathcal{H}_{\rm VDW} + \mathcal{H}_{\rm hfs}$.

$\mathcal{H}_{\rm VDW}$ is the van der Waals interaction Hamiltonian given by

$$\mathcal{H}_{\rm VDW} = (e^2/R^3)\sum_{\lambda,\,\nu}(2z^A_\lambda z^B_\nu - x^A_\lambda x^B_\nu - y^A_\lambda y^B_\nu) + [\text{terms in } (1/R^4)\,,\ (1/R^5), \ldots] \quad , \tag{4}$$

where the summations λ and ν are over the electrons belonging to atoms A and B, respectively. $\mathcal{H}_{\rm hfs}$ is the Fermi-contact Hamiltonian for the atom A, namely,

$$\mathcal{H}_{\rm hfs} = (16\pi/3I_A)\,\mu^A_N\,\beta\,\vec{\rm I}_A\cdot\sum_\lambda \vec{\rm s}_\lambda\,\delta(\vec{\rm r}^A_\lambda) \quad . \tag{5}$$

In Eq. (4) the first term is the dipole-dipole interaction, while the succeeding terms represent dipole-quadrupole, quadrupole-quadrupole, and higher-order multipole interactions. The electronic coordinates $\vec{\rm r}^A_\lambda(x^A_\lambda, y^A_\lambda, z^A_\lambda)$ are measured with respect to nucleus A and $\vec{\rm r}^B_\nu(x^B_\nu, y^B_\nu, z^B_\nu)$ are measured with respect to B. While in our present work we shall consider only the first term in Eq. (4), the process of calculation can easily be generalized to include other terms. In Eq. (5) $\vec{\rm I}_A$ and μ^A_N are the spin and magnetic moment of nucleus A, $\vec{\rm s}_\lambda$ is the spin angular momentum of the λth electron belonging to A, and β is the Bohr magneton $e\hbar/2mc$.

It has been shown elsewhere[4, 5] that the lowest order in which the change in hyperfine energy occurs for interacting atoms is third order (Δ^3E) in $\mathcal{H}'$. On extracting the terms linear in $\mathcal{H}_{\rm hfs}$ from the perturbation expansion for Δ^3E and using the angular momentum selection rules, the following expression for the change in hfs energy results, namely,

$$\Delta^3E_1 = 12/R^6 \sum_{i,j,k}{}' \frac{\langle\Psi_{0A}|Z^A|\Psi_{iA}\rangle\langle\Psi_{iA}|Z^A|\Psi_{jA}\rangle\langle\Psi_{jA}|\mathcal{H}_{\rm hfs}|\Psi_{0A}\rangle\,|\langle\Psi_{0B}|Z^B|\Psi_{kB}\rangle|^2}{(E^A_{0i}+E^B_{0k})E^A_{0j}} \quad , \tag{6}$$

$$\Delta^3E_2 = 6/R^6 \sum_{i,j,k}{}' \frac{\langle\Psi_{0A}|Z^A|\Psi_{iA}\rangle\langle\Psi_{iA}|\mathcal{H}_{\rm hfs}|\Psi_{jA}\rangle\langle\Psi_{jA}|Z^A|\Psi_{0A}\rangle\,|\langle\Psi_{0B}|Z^B|\Psi_{kB}\rangle|^2}{(E^A_{0i}+E^B_{0k})(E^A_{0j}+E^B_{0k})} \quad , \tag{7}$$

and

$$\Delta^3E_3 = -6/R^6\langle\Psi_{0A}|\mathcal{H}_{\rm hfs}|\Psi_{0A}\rangle\sum_{i,j}{}' \frac{|\langle\Psi_{0A}|Z^A|\Psi_{iA}\rangle|^2\,|\langle\Psi_{0B}|Z^B|\Psi_{jB}\rangle|^2}{(E^A_{0i}+E^B_{0j})^2} \quad . \tag{8}$$

The quantity of interest to us is the fractional shift $\Delta\mathcal{A}(R)/\mathcal{A}_0$ which is given by

$$\frac{\Delta\mathcal{A}(R)}{\mathcal{A}_0} = \frac{\Delta^3E_1+\Delta^3E_2+\Delta^3E_3}{\langle\Psi_{0A}|\mathcal{H}_{\rm hfs}|\Psi_{0A}\rangle} = \frac{1}{R^6}(D_1+D_2+D_3) \ , \tag{9}$$

where $\mathcal{A}_0$ is the hyperfine structure constant of the isolated atom A. In Eqs. (6)–(9), Ψ_{0A} and Ψ_{0B} refer to the exact ground-state wave functions of the individual atoms A and B at infinite separation. The symbols E^A_{0i} and E^B_{0k} represent the excitation energies: $E^A_{0i} = E^A_0 - E^A_i$, $E^B_{0k} = E^B_0 - E^B_k$. In Eqs. (6)–(8), Z^A and Z^B are given by

$$Z^A = \sum_\lambda z^A_\lambda, \quad Z^B = \sum_\nu z^B_\nu \quad , \tag{10}$$

and may be regarded as the total dipole operators for the atoms A and B. The primes on the summations in Eqs. (6)–(8) indicate that in the summations over the states i,j of atom A and k of atom B, only excited states have to be included.

For our present purposes, it is convenient to express the shift of the hyperfine energy given in Eqs. (6)–(8) in terms of integrals over imaginary frequencies. Thus, using the well-known relation

$$1/(a+b) = (2/\pi)\int_0^\infty (ab\,d\omega)/(a^2+\omega^2)(b^2+\omega^2)$$

we can rewrite the expressions in Eqs. (6)–(8) as

$$\Delta^3 E_1 = (6/\pi R^6)\int_0^\infty d\omega\, F_1^A(i\omega)\alpha^B(i\omega) \quad , \tag{11}$$

$$\Delta^3 E_2 = (3/2\pi^2 R^6)\int_0^\infty d\omega_1 \int_0^\infty d\omega_2 F_2^A(i\omega_1, i\omega_2)\beta^B \times(i\omega_1, i\omega_2) \quad , \tag{12}$$

$$\Delta^3 E_3 = -\frac{3}{2\pi^2 R^6}\alpha_0 \int_0^\infty d\omega_1 \int_0^\infty d\omega_2 \beta^A(i\omega_1, i\omega_2) \times \beta^B(i\omega_1, i\omega_2) \quad , \tag{13}$$

where the response functions $F_1^A, F_2^A, \beta^A, \beta^B$, and α^B are similar to the response functions in polarizability calculations[3, 6, 7] and are defined by the relations:

$$F_1^A(\omega) = 2\langle \Psi_{0A}^{(2)}(\omega)|\mathcal{H}_{\text{hfs}}|\Psi_{0A}(\omega)\rangle = 2\sum_{i,j}{}' \frac{\langle\Psi_{0A}|Z^A|\Psi_{iA}\rangle\langle\Psi_{iA}|Z^A|\Psi_{jA}\rangle E_{0i}^A\langle\Psi_{jA}|\mathcal{H}_{\text{hfs}}|\Psi_{0A}\rangle}{[(E_{0i}^A)^2-\omega^2]E_{0j}^A} \quad , \tag{14}$$

$$F_2^A(\omega_1,\omega_2) = 2\langle \Psi_{0A}^{(1)}(\omega_1)|\mathcal{H}_{\text{hfs}}|\Psi_{0A}^{(1)}(\omega_2)\rangle = 2\sum_{i,j}{}' \frac{\langle\Psi_{0A}|Z^A|\Psi_{iA}\rangle E_{0i}^A\langle\Psi_{iA}|\mathcal{H}_{\text{hfs}}|\Psi_{jA}\rangle\langle\Psi_{jA}|Z^A|\Psi_{0A}\rangle E_{0i}^A}{[(E_{0i}^A)^2-\omega_1^2][(E_{0j}^A)^2-\omega_2^2]} \quad , \tag{15}$$

$$\beta^A(\omega_1,\omega_2) = 4\langle \Psi_{0A}^{(1)}(\omega_1)|\Psi_{0A}^{(1)}(\omega_2)\rangle = 4\sum_i{}' \frac{\langle\Psi_{0A}|Z^A|\Psi_{iA}\rangle\langle\Psi_{iA}|Z^A|\Psi_{0A}\rangle(E_{0i})^2}{[(E_{0i}^A)^2-\omega_1^2][(E_{0i}^A)^2-\omega_2^2]} \quad , \tag{16}$$

$$\beta^B(\omega_1,\omega_2) = 4\langle \Psi_{0B}^{(1)}(\omega_1)|\Psi_{0B}^{(1)}(\omega_2)\rangle = 4\sum_i{}' \frac{\langle\Psi_{0B}|Z^B|\Psi_{iB}\rangle\langle\Psi_{iB}|Z^B|\Psi_{0B}\rangle(E_{0i}^B)^2}{[(E_{0i}^B)^2-\omega_1^2][(E_{0i}^B)^2-\omega_2^2]} \quad , \tag{17}$$

$$\alpha_B(\omega) = 2\langle \Psi_{0B}(\omega)|Z^B|\Psi_{0B}^{(1)}(\omega)\rangle = 2\sum_j{}' \frac{\langle\Psi_{0B}|Z^B|\Psi_{jB}\rangle\langle\Psi_{jB}|Z^B|\Psi_{0B}\rangle E_{0j}^B}{(E_{0j}^B)^2-\omega^2} \quad . \tag{18}$$

In Eqs. (14)–(18), $\Psi_{0A}^{(1)}(\omega)$ and $\Psi_{0A}^{(2)}(\omega)$ represent first- and second-order perturbed wave functions for atom A due to the external field defined by

$$\Psi_{0A}^{(1)}(\omega) = \sum_i \frac{\langle\Psi_{0A}|Z^A|\Psi_{iA}\rangle E_{0i}}{(E_{0i}^A)^2-\omega^2}\,|\Psi_{iA}\rangle \quad , \tag{19}$$

$$\Psi_{0A}^{(2)}(\omega) = \sum_j{}' \frac{E_{0i}^A\langle\Psi_{0A}|Z^A|\Psi_{iA}\rangle\langle\Psi_{iA}|Z^A|\Psi_{jA}\rangle}{E_{0j}^A[(E_{0i}^A)^2-\omega^2]}\,|\Psi_{jA}\rangle . \tag{20}$$

The first-order perturbed wave function $\Psi_{0B}^{(1)}(\omega)$ is defined in the same way as $\Psi_{0A}^{(1)}(\omega)$ in Eq. (19), with the index A replaced by B to refer to atom B. The function $\alpha^B(\omega)$ is the familiar frequency-dependent polarizability that is used in the VDW energy calculation.[1] The development of the many-body formalism for handling these additional response functions follows broadly similar lines as those for $\alpha^B(\omega)$. However, some additional considerations are necessary in view of the greater complexity of the form compared to $\alpha^B(\omega)$. The many-body theory for calculating these response functions will be sketched in the remainder of this section.

In Eqs. (11)–(15) for the response functions, the hyperfine operator occurs only in the expectation value expressions. The situation is thus broadly analogous to that in the theory of hyperfine constant of isolated atoms, except that we now need atomic wave functions perturbed by a time-dependent external field. Since the ground-state wave functions Ψ_{0A} for the atom A are not known exactly, one has to start as usual with the zero-order wave function Φ_{0A} (and Φ_{0B}), which is an eigenfunction of the zero-order Hamiltonian $\mathcal{H}_{0A}$ and handle both the difference $\mathcal{H}_{1A}'$ between the actual Hamiltonian $\mathcal{H}_A$ and $\mathcal{H}_{0A}$ and the electric field Hamiltonian $\mathcal{H}_2'(t)$ as perturbations, and make use of the double-perturbation formalism. The same procedure is applied to obtain the ground-state wave function Ψ_{0B} for atom B. For the sake of uniformity, we use notations similar to that in the calculation of $\alpha(\omega)$,[7] namely;

$$\mathcal{H}_0 = \sum_i (T_i + V_i) = \sum_i \epsilon_i \eta_i^\dagger \eta_i \, , \tag{21}$$

with $T_i = -\frac{1}{2}\nabla_i^2 - N/r_i$, (22)

$$\mathcal{H}' = \mathcal{H}_1' + \mathcal{H}_2'(t) \quad , \tag{23}$$

$$\mathcal{H}_1' = \sum_{i,j,k,l}{}' \langle ij|(1/r_{12})|kl\rangle \eta_i^\dagger\eta_j^\dagger\eta_l\eta_k - \sum\langle i|V|j\rangle \times\eta_i^\dagger\eta_j \quad , \tag{24}$$

and $\mathcal{H}_2'(t) = \sum_{i>j} (\mathcal{E}_0\langle i|z|j\rangle e^{i\omega t} + \text{c.c.})\eta_i^\dagger\eta_j$, (25)

where $2\mathcal{E}_0$ is the amplitude of the external electromagnetic field. We have omitted suffix A in the above expressions, since we are dealing with atoms A and B individually. The wave function $\Psi(t)$ for the atom, incorporating the combined effects of $\mathcal{H}_1'$ and $\mathcal{H}_2'$ can be written in the interaction representation in the form

$$\Psi(t)=\lim_{\alpha\to 0} U^{\alpha}(t,-\infty)\Phi_0 , \tag{26}$$

where

$$U^{\alpha}(t,t_0)=1+\sum_{n=1}^{\infty} U_n^{\alpha}(t,t_0) , \tag{27}$$

$$U_n^{\alpha}(t,t_0)=[(-i)^n/n!]\int_{t_0}^{t} dt_1\cdots \times\int_{t_0}^{t} dt_n T[\mathcal{H}_{I_\alpha}'(t_1)\cdots\mathcal{H}_{I_\alpha}'(t_n)] , \tag{28}$$

and

$$\mathcal{H}_{I_\alpha}'(t)=e^{-i\mathcal{H}_0 t}\mathcal{H}'(t)e^{i\mathcal{H}_0 t}e^{-\alpha|t|} . \tag{29}$$

In performing the time integrations in Eq. (28) one utilizes the usual limiting procedures described by Eq. (30):

$$\int_{-\infty}^{t} e^{i\omega t}dt=\lim_{\alpha\to 0^+}\int_{-\infty}^{t} e^{(\alpha+i\omega)t}dt=e^{i\omega t}/i\omega . \tag{30}$$

Thus, Eq. (26) for $\Psi(t)$ becomes

$$\begin{aligned}\Psi(t)=&\sum_{n=0}^{\infty} e^{i(\mathcal{H}_0-E_0)t}\frac{1}{E_0-\mathcal{H}_0}\mathcal{H}_1'\frac{1}{E_0-\mathcal{H}_0}\mathcal{H}_1'\cdots\mathcal{H}_1'\frac{1}{E_0-\mathcal{H}_0}\mathcal{H}_1'\Phi_0+\sum_{n=0}^{\infty} e^{i(\mathcal{H}_0-E_0\pm\omega t)}\frac{1}{E_0-\mathcal{H}_0\mp\omega}\mathcal{H}_1'\cdots\\ &\times\mathcal{H}_1'\frac{1}{E_0-\mathcal{H}_0\mp\omega}\mathcal{E}_0 z\Phi_0\\ &+\sum_{n=0}^{\infty} e^{i(\mathcal{H}_0-E_0\pm 2\omega)t}\frac{1}{E_0-\mathcal{H}_0\mp 2\omega}\mathcal{H}_1'\cdots\mathcal{H}_1'\frac{1}{E_0-\mathcal{H}_0\mp 2\omega}\mathcal{E}_0 z\frac{1}{E_0-\mathcal{H}_0\mp\omega}\mathcal{E}_0 z\Phi_0\\ &+\sum_{n=0}^{\infty} e^{i(\mathcal{H}_0-E_0)t}\frac{1}{E_0-\mathcal{H}_0}\mathcal{H}_1'\cdots\mathcal{H}_1'\frac{1}{E_0-\mathcal{H}_0}\mathcal{E}_0 z\frac{1}{E_0-\mathcal{H}_0\mp\omega}\mathcal{E}_0 z\Phi_0\\ &+\sum_{n=0}^{\infty} e^{i(\mathcal{H}_0-E_0\pm 3\omega)t}\frac{1}{E_0-\mathcal{H}_0\mp 3\omega}\mathcal{H}_1'\cdots\mathcal{H}_1'\frac{1}{E_0-\mathcal{H}_0\mp 3\omega}\mathcal{E}_0 z\frac{1}{E_0-\mathcal{H}_0\mp 2\omega}\mathcal{E}_0 z\frac{1}{E_0-\mathcal{H}_0\mp\omega}\mathcal{E}_0 z\Phi_0+\cdots .\end{aligned} \tag{31}$$

In the diagrammatic representation of various terms in Eq. (31) there will be two characteristic vertices associated with $\mathcal{H}_1'$ and $\mathcal{H}_2'(t)$. In the construction of the diagrams for $\Psi(t)$ and diagrams associated with the response functions, it is helpful to note that the time dependence connected with $\mathcal{H}_1'$ vertices does not involve the frequency, whereas each of the vertices associated with the operator $\mathcal{H}_2'(t)$ introduces characteristic frequencies ω and $-\omega$. Another point that should be noted here is that the normalization condition for $\Psi(t)$ is

$$\langle\Psi(t)|\Psi(t)\rangle=1 \tag{32}$$

in view of the unitarity[8] of the evolution operator U and the normalization of the zero-order function $\langle\Phi_0|\Phi_0\rangle=1$. Proceeding to the diagrammatic representation, typical terms in the perturbation expansion of $\Psi(t)$ involving one and two orders in $\mathcal{H}_1'$ and $\mathcal{H}_2'(t)$ can be represented as those in Fig. 1. Each of these diagrams actually represents the sum of a set of diagrams obtained by permuting over all the possible relative positions of the $\mathcal{H}_1'$ and $\mathcal{H}_2'(t)$ vertices, corresponding to similar permutations among the $\mathcal{H}_{I_\alpha}(t_i)$ terms in Eq. (28).

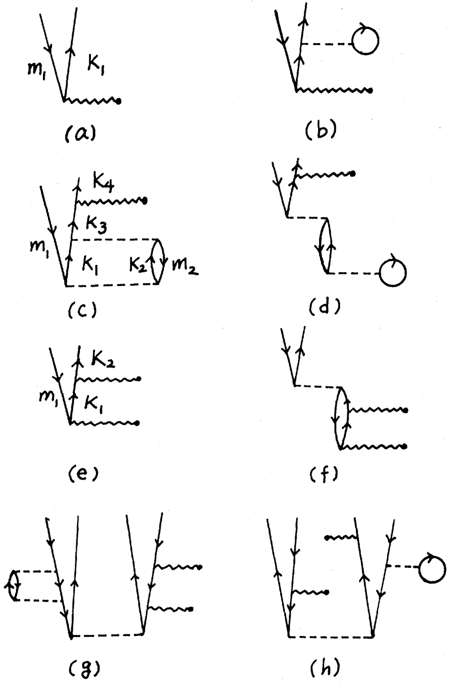

FIG. 1. Some diagrams for the perturbation expansion of the exact wave function $\Psi(t)$.

The rules for energy denominators are simply extensions of rules for the polarizability problem with an addition of a characteristic frequency $\pm\omega$ after each $\mathcal{H}_2'(t_i)$ vertex. In keeping with our convention used in Eqs. (19) and (20) in Sec. II, where exact wave functions of the time-dependent problem were being considered, one can define $\Psi_0^{(n)}$ to be the sum of all contributions to the wave function, in which the time-dependent perturbation acts n times while the number of $\mathcal{H}_1'$ interaction is unrestricted. In this sense, Figs. 1(a)–1(d) belong to $\Psi_0^{(1)}$, while 1(e)–1(h) belong to $\Psi_0^{(2)}$. Using the rules for the denominators and time dependence associated with the vertices, the algebraic expressions associated with Figs. 1(a), 1(c), and 1(e), for examples, can be shown to be, respectively:

Fig. 1(a),

$$-[\langle k_1|z|m_1\rangle/(\epsilon_{m_1}-\epsilon_{k_1}-\omega)e^{i\omega t}+\langle k_1|z|m_1\rangle/(\epsilon_{m_1}-\epsilon_{k_1}+\omega)e^{-i\omega t}]\,\mathcal{E}_0\eta_{k_1}^\dagger\eta_{m_1}\Phi_0\;;$$

Fig. 1(c),

$$-\left[\frac{\langle k_4|z|k_3\rangle\langle k_3m_2|r_{12}^{-1}|k_1k_2\rangle\langle k_1k_2|r_{12}^{-1}|m_1m_2\rangle}{(\epsilon_{m_1}-\epsilon_{k_4}-\omega)(\epsilon_{m_1}-\epsilon_{k_3})(\epsilon_{m_1}+\epsilon_{m_2}-\epsilon_{k_1}-\epsilon_{k_2})}\,\mathcal{E}_0e^{i\omega t}+(\text{same term with }\omega\rightarrow-\omega)\right]$$

$$\times\eta_{k_4}^\dagger\eta_{k_3}\eta_{k_3}^\dagger\eta_{k_1}\eta_{k_2}\eta_{m_2}^\dagger\eta_{k_2}^\dagger\eta_{k_1}^\dagger\eta_{m_2}\eta_{m_1}\Phi_0\;;$$

Fig. 1(e),

$$-[\langle m_1|z|k_1\rangle\langle k_1|z|k_2\rangle e^{\pm 2i\omega t}/(\epsilon_{m_1}-\epsilon_{k_1}\mp\omega)(\epsilon_{m_1}-\epsilon_{k_2}\mp 2\omega)+\langle m_1|z|k_1\rangle\langle k_1|z|k_2\rangle/(\epsilon_{m_1}-\epsilon_{k_1}\mp\omega)(\epsilon_{m_1}-\epsilon_{k_1})]$$

$$\times\mathcal{E}_0^2\eta_{k_2}^\dagger\eta_{k_1}\eta_{k_1}^\dagger\eta_{m_1}\Phi_0\;.$$

The sign in front of each of the expressions is obtained from the usual rules for many-body diagrams.[9] Thus, the combination of sets of diagrams similar to those in Fig. 1 yield the perturbed wave functions $\Psi_{0A}^{(1)}$ and $\Psi_{0A}^{(2)}$, which occur in Eqs. (14)–(18). To evaluate the response functions F_1^A, F_2^A, β^A, and β^B, we then have to calculate the matrix elements in Eqs. (14)–(17). In diagrammatic language we thus have to construct the appropriate diagrams for the response functions using the wave function diagrams $\Psi_{0A}^{(1)}, \Psi_{0A}^{(2)}$ and introducing the necessary vertex represented by a wiggly line terminating with a triangle for $\mathcal{H}_{\text{hfs}}$ at the requisite location. A few additional remarks are appropriate here before proceeding to response function diagrams. First, from Eqs. (14)–(18), $\mathcal{H}_2'(t)$ vertices are expected to occur twice in the diagrams for all five response functions involved, albeit in different relative locations for different diagrams. Since these functions are real and time-independent, the two vertices associated with the two $\mathcal{H}_2'(t)$ bear a complex-conjugate relationship to each other, namely $\mathcal{E}_0ze^{i\omega t}$ and $\mathcal{E}_0ze^{-i\omega t}$, respectively. Second, in view of the normalization condition in Eq. (32), all the response functions are expected to involve linked diagrams as in earlier work on the polarizability of neon.[7]

Figures 2–4 represent some typical diagrams for response functions F_1^A, F_2^A, and β^B. The diagrams for the polarizability $\alpha^B(\omega)$ are the same

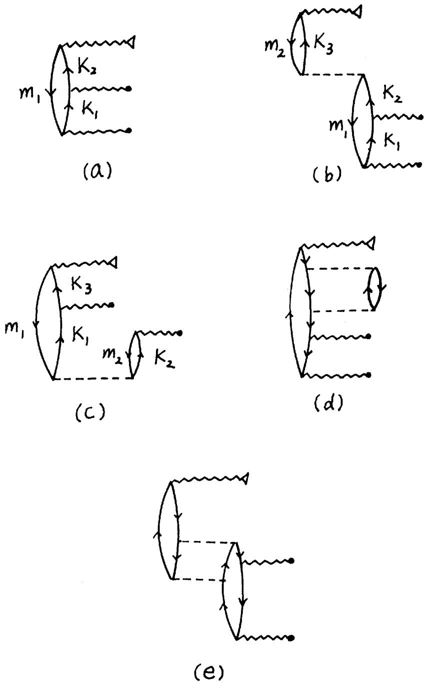

FIG. 2. Some typical diagrams for the response function F_1^A.

as those already discussed in our earlier work on $\alpha(\omega)$ for neon[7] and helium,[3] and will not be repeated here. The algebraic expressions that correspond to these diagrams can be written down using the rules discussed for the wave function diagrams. A few of the expressions corresponding to Figs. 2(a), 2(b), and 2(c) are presented here, respectively, as:

Fig. 2(a),

$$\sum{}' \langle m_1|\mathcal{H}_{\text{hfs}}|k_2\rangle \langle k_2|Z^A|k_1\rangle \langle k_1|Z^A|m_1\rangle \epsilon^A_{m_1k_1}/\epsilon^A_{m_1k_2}[(\epsilon^A_{m_1k_1})^2-\omega^2] \;;$$

Fig. 2(b),

$$\sum{}' \frac{\langle m_2|\mathcal{H}_{\text{hfs}}|k_3\rangle}{\epsilon^A_{m_2k_3}} \cdot \frac{\langle m_1k_3|(r_{12})^{-1}|k_2m_2\rangle \langle k_2|Z^A|k_1\rangle \langle k_1|Z^A|m_1\rangle \epsilon^A_{m_1k_1}}{[\epsilon^A_{m_1k_2}+\epsilon^A_{m_2k_3}][(\epsilon^A_{m_1k_1})^2-\omega^2]} \;;$$

Fig. 2(c),

$$\sum{}' \langle m_1|\mathcal{H}_{\text{hfs}}|k_3\rangle/\epsilon^A_{m_1k_3}\cdot\langle k_3|Z^A|k_1\rangle \langle m_2|Z^A|k_2\rangle \langle k_1k_2|\frac{1}{r_{12}}|m_1m_2\rangle \epsilon^A_{m_1k_1}/[\epsilon^A_{m_1k_1}+\epsilon^A_{m_2k_2}][(\epsilon^A_{m_1k_1})^2-\omega^2] \;,$$

where $\epsilon^A_{mk}=\epsilon^A_m-\epsilon^A_k$.

To make the distinction between F_1^A given by Eq. (14) and other response functions F_2^A and β^A in Eqs. (15) and (16) with respect to the additional denominator involving ω, which occurs in the latter, we have drawn the diagrams in Fig. 2 somewhat differently from the diamond shaped ones for others. In the expressions for the diagrams, the summation implies sum over discrete excited states and integration over the continuum. As in earlier work,[1,3,6,7,9] the basis set is generated by the zero-order Hamiltonian corresponding to the restricted Hartree-Fock and V^{N-1} potential. Since the response functions that occur in Eqs. (11)–(13) involve the imaginary frequency $i\omega$ in place of ω, we have to replace ω_1^2 and ω_2^2 by $-\omega_1^2$ and $-\omega_2^2$, respectively, in Eqs. (14)–(18).

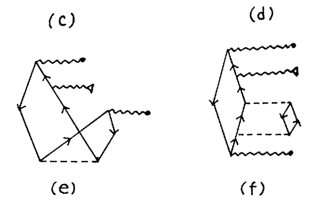

FIG. 3. Some typical diagrams for the response function F_2^A.

III. RESULTS AND DISCUSSION

The method of evaluation of diagrams discussed in Sec. II. is very similar to that used for time-independent and time-dependent properties of atoms in earlier literature.[1,3,6,7,9] The basis-set wave functions and eigenvalues for hydrogen, helium, and neon with V^{N-1} potentials were all taken from earlier work on polarizabilities. We remark here that the response function $F_1^A(\omega)$ could have been evaluated exactly by recasting it in the form

$$F_1^A(\omega)=2\langle\Psi_{0A}^{(1)}(\omega)|Z_A(\mathcal{E}_0e^{i\omega t}+\mathcal{E}_0e^{-i\omega t})|\Psi_{0AN}^{(1)}(\omega)\rangle \;,$$

where $\Psi_{0A}^{(1)}(\omega)$ is the first-order perturbed wave function due to the external perturbation $\mathcal{H}_2'(t)$ and $\Psi_{0AN}^{(1)}$ is the first-order perturbed wave function due

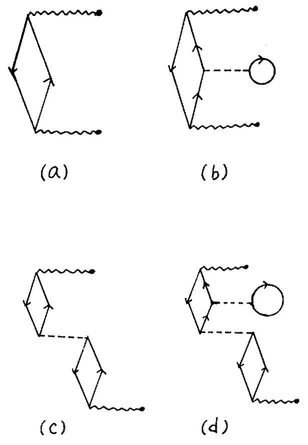

FIG. 4. Some typical diagrams for the response functions β^A and β^B.

to the Fermi contact operator $\mathcal{H}_{\text{hfs}}$. An exact solution can be derived from this and is known in the literature.[10] However, in line with our earlier work[1] for VDW forces involving the hydrogen atom, where the result obtained by BG method is in excellent agreement with the exact VDW coefficient, we have also utilized here the usual BG expansion in terms of the basis set. This procedure is easily extendable to more complex atom where an exact solution for F_1^A is not obtainable. In addition to this term, we get a further contribution from the third term. The second term does not make any contribution since it involves the excitation of a 1*s* electron of hydrogen atom to the *p* orbitals, where the Fermi contact hfs matrix element vanishes. For both α^B and β^B, which involve polarizabilities of helium and neon atoms, diagrams involving up to the second order of $\mathcal{H}_1'$ were utilized in the calculation. Second-order effects in $\mathcal{H}_1'$ have already been shown to be sufficient in VDW calculations in helium[1] and earlier work on the dynamic polarizability of neon.[7] Our calculated results for VDW constant C involving H-Ne and Ne-Ne are presented in Table I where, for the sake of completeness, we have also included $C_{\text{H-H}}$, $C_{\text{H-He}}$, and $C_{\text{He-He}}$ from earlier work.[1] A critical comparison of the results of VDW constants in the latter three systems with experiment and other calculations has been presented earlier.[1] There appears to be some difference between our results for $C_{\text{H-Ne}}$, $C_{\text{He-Ne}}$, $C_{\text{Ne-Ne}}$, and the most recent semiempirical values obtained by Davison,[11] which utilized experimental oscillator strengths to evaluate the matrix elements involved for the first few excited states in perturbation sum and approximated the rest of the perturbation series through the use of the dipole sum rule. This approximation is likely to be the main source of the discrepancy between his and our results. We believe that the excellent agreement noted earlier[3,7] between our calculated refractive indices and experiment testifies to the accuracy of the VDW constants we have obtained.

TABLE I. van der Waals constants C_{AB} between interacting atoms A and B in a.u.[a]

A B	H	He	Ne
H	6.499	2.820	5.794
He	2.820	1.50	3.399
Ne	5.794	3.399	6.925

[a] All values are in atomic units $(e^2a_0^5)$.

Our results for the long-range hyperfine pressure shift parameters $D_{\text{H-He}}$ and $D_{\text{H-Ne}}$ are presented in Table II together with the values obtained by earlier variational calculations[12] and semiempirical results of Davison.[11] The contribution to D is composed of D_1 and D_3 referring to the first and the third terms in the expression (9). D_3 is small compared to D_1 in both cases, in keeping with a similar conclusion from variational[4,13] and semiempirical results.[11,14] D_1 involves F_1^A and α^B, and the relative contributions of various possible diagrams to α^B have already been discussed.[3,7] In the case of hydrogen, F_1^A involves only a single diagram since we have only one electron to consider. The other diagrams in Fig. 2 would make finite contributions if we had more than one electron; these and other additional diagrams would take account of core polarization and correlation effects as in the case of isolated atoms. The expression for D_3 involves $\beta^A(\omega_1, \omega_2)$ and $\beta^B(\omega_1, \omega_2)$. For these latter functions in hydrogen atoms, only the first diagram in Fig. 4 survives; for helium and neon, the relative contributions from these latter diagrams compared to the first one in Fig. 4, are much smaller than in the case of similar diagrams for $\alpha^B(\omega)$,[3,7] presumably because of the occurrence of additional energy denominators in $\beta^B(\omega_1, \omega_2)$ diagrams.

Our final results are in satisfactory agreement with both variational[13] and semiempirical results.[11] The agreement with variational calculation indicates that the variational function chosen was reasonably adequate at least for the present systems. A deeper insight into the relationship between the

TABLE II. Coefficients of the fractional frequency shift of atomic hydrogen in inert gases.[a]

System	H-He			H-Ne		
Method	$-D_1$	$-D_3$	$-D=-(D_1+D_3)$	$-D_1$	$-D_3$	$-D=-(D_1+D_3)$
One-electron variational[b]	12.20	2.07	14.27	23.67	3.36	27.03
Present work						
One-electron	12.334	2.137	14.471	23.264	3.488	26.752
Final results with consistency and correlation	11.419	1.918	13.337	22.710	3.420	26.130
Semiempirical[c]	11.36	1.90	13.26	22.5	3.4	25.9

[a] See Eqs. (6)–(9). [b] See Ref. 13. [c] See Ref. 11.

present calculation and the variational results may be obtained by collecting the contributions from the diagrams for α^B and β^B, which represent purely one-electron effects and computing D using these contributions. These results are presented in the second row of Table II. One notes that these one-electron contributions are in better agreement with variational results[13] than those including many-body effects. While it is difficult to pinpoint the reason for the remaining difference between one-electron-diagram contributions and variational results, part of the source could be that small uncertain amounts of correlation may be included in the variational function due to the form of the variational function chosen.

The semiempirical results[11] are in better agreement with our values of D including correlation effects, the agreement being much better than in the case of VDW constants referred to earlier. This situation does appear somewhat puzzling. A possible way out of the dilemma is through noting that whereas the approximate use of the sum rule involving oscillator strengths was applied twice by Davison[11] in the VDW constant calculation, it was only applied once in the HPS calculation to α^B in Eq. (11), F_1^A being calculated by the exact solution $\Psi_{0AN}^{(1)}(\omega)$ and variationally determined by $\Psi_{0A}^{(1)}(\omega)$. The comparison between Davison's results and ours thus indicates that one can use his results for D in H-Ar, H-Kr, and H-Xe with greater confidence than the corresponding semiempirical VDW constants.

In summary, we have presented a procedure for calculation of the long-range hyperfine frequency shift due to VDW interaction, without resort to any semiempirical assumptions. The present method allows the separation of one-electron and many-electron effects in a systematic manner so that the relative importance of these effects can be assessed in a manner similar to the manner used in assessing the properties of isolated atoms.[9, 15–17] Thus, one of the uncertainties in earlier pressure-shift calculations[4] has been removed, namely the role of intraatomic correlation effects on the long-range contribution to the frequency shift. Also, the procedure can be easily extended to include contributions from higher-multipole interactions between atoms to the hyperfine frequency shift. The remaining stumbling block to quantitative calculation of HPS is the lack of a proper treatment of the shift in the short and intermediate ranges so that the arbitrary cutoff procedure used in statistical averaging[4, 13] over interatomic separations may be dispensed with.

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