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FREQUENCY-DEPENDENT MULTIPOLE POLARIZABILITIES OF ATOMIC SYSTEMS

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Abstract. — A variational calculation for frequency dependent multipole polarizabilities of atomic systems is proposed; for zero frequency it reduces to our previous formalism of the static case. This present scheme has been applied to obtain the dispersion energy between interacting hydrogen and helium pairs. Our results are in harmony with others.

The calculation of multipole polarizabilities was initiated by the use of single [1] and double [2] perturbation theory. Recently Rivail and Rinaldi [3] have proposed an alternative single perturbation theory applicable to static multipole polarizabilities of atomic systems. We have already generalized [4] this scheme. In this procedure the total energy of the atomic system is expressed in terms of expansions involving induced multipole moments so that the static multipole polarizabilities are obtained as second order derivatives of the total energy w.r.t. \( P_l^m \), \( P_l^m \) being the associated Legendre polynomial. Furthermore, Rivail and Rinaldi’s work was based on the variational calculation with one variational constant in the perturbed wave function while we took an appropriate number of variational constants till convergence was achieved in static multipole polarizabilities.

The schemes [3, 4] are parallel to the method of single perturbation [1] or double perturbation [2], if not identical. In the present communication we extend such [4] a scheme to incorporate the frequency-dependent multipole polarizabilities of atomic systems. We propose the following expansion for the total energy, the applied electric field being harmonic in time with angular frequency \( \omega \),

\[
E = \frac{E(\omega) + E(-\omega)}{2} = E_0 + \frac{Z'(Z-N)}{\gamma^2} \sum_{l=1}^{\infty} F_l S_l - \frac{1}{4} \sum_{l=1}^{\infty} F_l \bar{\alpha}_l(\omega). F_l ,
\]

in the notation of earlier references [3, 4], \( \alpha_l(\omega) \) being the frequency dependent multipole polarizability and

\[
\bar{\alpha}_l(\omega) = \alpha_l(+\omega) + \alpha_l(-\omega) .
\]

Note that for \( \omega = 0 \), the expression (1) reduces to the static expression [3, 4]. We outline the procedure to work out \( \alpha_l(\omega) \) by taking the perturbed wave function as

\[
\Psi(\pm) = N_l(\pm) \Psi_0(1 + \lambda_l(\pm \omega) S_l)
\]

for one variational constant. Note that the variational constant \( \lambda_l \) depends on frequency.

Rewrite \( \Psi(\pm) \) as

\[
\Psi(\pm) = \Phi_0 + \chi_l(\pm)
\]

\[
\Phi_0 = N_l(\pm) \Psi_0
\]

\[
\chi_l(\pm) = N_l(\pm) \lambda_l(\pm \omega) S_l \Psi_0
\]
Now, $E(\pm w)$ as defined below is minimized w.r.t. variational constant $\lambda_1(\pm w)$, subject to normalization

$$<\Psi(\pm)|\Psi(\pm)> = 1.$$ \hfill (5)

$$E(\pm w) = <\Psi(\pm)|H_0 - S_i F_i|\Psi(\pm)> + <\lambda(\pm)|\pm w|\chi(\pm)>.$$ \hfill (6)

We obtain

$$E(\pm w) = E_0 + \frac{\lambda_1^{2}(\pm w)}{4} - 2 \lambda_1(\pm w) <S_i^2>F_i \pm w \lambda_1^{2}(\pm w)<S_i^2> - F_i<\lambda_i> + 2 \lambda_1(\pm w)<S_i^2>F_i$$ \hfill (7)

$$\lambda_1(\pm w) = \frac{4 F_i[S_i^2 - <S_i^2>]}{<S_i^2> \pm 4 w <S_i^2>}.$$ \hfill (8)

Substituting for $\lambda_1(\pm w)$ in (7) we have

$$E(\pm w) = E_0 - F_i<\lambda_i> - \frac{1}{4} \frac{[4 <S_i^2> - <S_i^2>]^2}{4 <S_i^2> \pm 4 w <S_i^2>} F_i$$ \hfill (9)

$\chi(\pm)$ has the following expression

$$\chi(\pm) = \frac{1}{1 - A_{1L} w^2}.$$ \hfill (10)

For two variational constants,

$$\chi(\pm) = N(\pm) \Psi_0[\lambda_1(\pm w) S_i + \gamma h(\pm w) S_i]$$ \hfill (12)

the minimization of $E(\pm w)$ w.r.t. $\lambda_1(\pm w)$ and $h(\pm w)$ as given by eq. (6) with $\chi(\pm)$ given by (12) yields

$$\lambda_1(\pm w) = C_1(\pm w) F_i$$ \hfill (13)

$$h(\pm w) = C_2(\pm w) F_i$$

where $C_1(\pm w)$ and $C_2(\pm w)$ are solutions of the following matrix equation,

$$\begin{bmatrix}
\frac{1}{2} <\nabla^2 S_i^2> \pm 2 w <S_i^2> \\
<S_i^2> \pm 2 w <S_i^2> \\
<S_i^2> \pm 2 w <S_i^2>
\end{bmatrix}
= \begin{bmatrix}
C_1(\pm w) \\
C_2(\pm w) \\
2 <S_i^2>
\end{bmatrix}.$$ \hfill (14)

Using equations (12) to (14) in (6) we get

$$E(\pm w) = E_0 - F_i<S_i> - \frac{1}{4} F_i[2 C_1(\pm w) <S_i^2> + 2 C_2(\pm w) <\gamma S_i^2>]$$ \hfill (15)

$$\chi(\pm) = [C_1(+ w) + C_1(- w)] <S_i^2> + [C_2(+ w) + C_2(- w)] <\gamma S_i^2>$$ \hfill (16)

which simplifies to

$$\chi(\pm) = \chi(0) \left\{ \frac{1 + S_{1L} w^2}{1 + P_{1L} w^2 + P_{2L} w^2} \right\}.$$ \hfill (17)

Note that $\chi(0)$ are static multipole polarizabilities; they have the same expression as in our earlier communication [4]. We write down values of $\chi(0)$ and other expressions in (17) as

$$\chi(0) = \frac{2 D_1 <S_i^2> + 2 D_2 <\gamma S_i^2>}{A}$$

$$S_{1L} = \frac{2 D_4 D_5 <S_i^2> + 2 D_1 D_3 <S_i^2>}{\chi(0) A^2}$$

$$P_{1L} = \frac{D_2^2}{A^2}$$

$$P_{2L} = \frac{D_2^2}{A^2}$$

$$A = \frac{1}{2} <\nabla^2 S_i^2> \pm <\nabla \gamma S_i, \nabla \gamma S_i> - <\nabla \gamma S_i, \nabla \gamma S_i>$$

$$D_1 = 2 <S_i^2> <\nabla \gamma S_i, \nabla \gamma S_i> - 2 <\gamma S_i^2> <\nabla \gamma S_i, \nabla \gamma S_i>$$

$$D_2 = <\nabla^2 S_i^2> <\gamma S_i^2> - 2 <S_i^2> <\nabla \gamma S_i, \nabla \gamma S_i>$$

$$D_3 = 4 <\gamma S_i^2> - 4 <S_i^2> <\gamma^2 S_i^2>$$

$$D_4 = \frac{1}{2} <\nabla^2 S_i^2> <\gamma^2 S_i^2> + \frac{1}{2} <S_i^2> <\nabla \gamma S_i, \nabla \gamma S_i> - 4 <\gamma S_i^2> <\nabla \gamma S_i, \nabla \gamma S_i>$$

$$D_5 = 4 <\gamma^2 S_i^2> <S_i^2> - 4 <\gamma S_i^2>.$$
Considering $n$ variational constants in the perturbed wave function implies the following choice for $\chi_i(\pm)$:

$$\chi_i(\pm) = N_i(\pm) \Psi_0[\lambda_i(\pm w) S_i + \gamma b_i(\pm w) S_i + \gamma^2 b_i(\pm w) S_i + \cdots]$$

(18)

where there are $n$ constants $\lambda_i(\pm w)$, $b_i(\pm w)$, $b_i(\pm w)$, ... Minimizing eq. (6) w.r.t. $n$ constants $\lambda_i(\pm w)$, $b_i(\pm w)$, ... and using $\chi_i(\pm)$ as given by (18), we get

$$\chi_i(w) = \chi_i(0) - \frac{1}{1 + \sum_{n=1}^{N} S_{nl} w^{2n}}$$

(19)

which is the $[N, N-1]$ Padé approximant for $\chi_i(w)$ [5]. Note that, now, $S_{nl}$ and $P_{nl}$ have cumbersome expressions unlike those for $n = 1$ and 2 as given above by eqs. (11) and (17) respectively.

We work out $\chi_i(w)$ for atomic hydrogen and He (our model for He is the same as in an earlier communication [4]) by using eq. (19) and varying the variational constants from 1 to 5. In Table I we list the dipole resonance frequencies for H and He (dipole case) while Table II contains the numerical values of the dipole polarizability of the He atom at imaginary frequency. We compare our results with earlier works. Our values of $\chi_i(iw)$ for the He atom (dipole case) are in harmony with those of Broussard and Kestner [2] because our model for $\chi_i(w)$ for the He atom is equivalent to a calculation using the uncoupled Hartree-Fock approximation, as in reference [2]. Our values for dipole resonance frequencies with 5 variational constants are in harmony with earlier works, both for H and He atom [6-9].

An important application of frequency-dependent multipole polarizability is to obtain the dispersion force coefficient for the long range interaction between two (or more) interacting neutral systems by utilizing the generalized Casimir-Polder integral formulas [5]

$$C(L_{a}, L_{b}) = \frac{2}{\pi} b(L_{a}, L_{b}) \int_{0}^{\infty} \chi_{i}(iy) \chi_{i}(iy) \, dy$$

(20)

where

$$b(L_{a}, L_{b}) = \frac{(2 L_{a} + 2 L_{b})}{4(2 L_{a} + 1)(2 L_{b} + 1)}$$

(21)

$\chi_{i}(iy)$ refers to frequency dependent multipole polarizabilities at an imaginary axis $w = iy$, the second order dispersion energy between two interacting systems is given by [10],

$$E_{2}(a - b) = - \frac{1}{R^{2}} \sum_{i} \sum_{j} \sum_{i} \sum_{j} \left( \frac{1}{R^{2L_{a} + L_{b} + 1}} \right) C(L_{a}, L_{b})$$

(22)

The following expression for the second-order dispersion energy for interacting hydrogen and He pairs results using eqs. (19) to (22)

$$E_{2}(H-H) = \frac{-6.496 \times 10^{-4}}{R^{6}} - \frac{124.3478}{R^{8}} - \frac{3.284604 \times 10^{4}}{R^{10}}$$

(23)

$$E_{2}(He-He) = \frac{-1.6625 \times 10^{-5}}{R^{6}} - \frac{14.6120}{R^{8}} - \frac{181.0412 \times 10^{5}}{R^{10}}$$

(24)
The corresponding expressions in earlier work are

\[
E_2(\text{H-H}) = -\frac{6.499}{R^6} - \frac{124.4}{R^8} - \frac{3.285}{R^{10}} \quad \text{(Dalgarno)}
\]

\[
= -\frac{6.499\,026}{R^6} - \frac{124.399\,008}{R^8} - \frac{3.285\,828}{R^{10}} \quad \text{(Bartolotti and Tyrrell)}
\]

\[
E_2(\text{He-He}) = -\frac{1.664}{R^6} - \frac{14.65}{R^8} - \frac{182.37}{R^{10}} \quad \text{(Broussard and Kestner)}.
\]

The present work is concluded with the remark that our values for \(E_2(\text{H-H})\) are in harmony with those of Dalgarno and Bartolotti et al. Note that we have worked out \(a_r(w)\) by taking only 5 variational constants. However, the slight discrepancy in our values for \(E_2(\text{H-H})\) and those of Dalgarno and Bartolotti et al. should be reduced by increasing the number of variational constants for \(a_r(w)\); our values for \(E_2(\text{He-He})\) are comparable with those of Broussard and Kestner [2] as both works use the uncoupled Hartree-Fock approximation. We are extending our scheme for the \(a_r(w)\) H atom [4] equivalent to the coupled Hartree-Fock approximation.

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References

[9] Atomic Energy Table (NBS), Circular No.