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# van der Waals interactions of $\Pi$ -state linear molecules with atoms. $C_6$ for $\text{NO}(X^2\Pi)$ interactions\*

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Formulas are derived for the van der Waals  $C_n$  coefficients for the interaction of a diatomic molecule in a  $\Pi$  electronic state with an  $S$ -state atom. Two triatomic states arise from the degenerate  $\Pi$  state. The average of the two energies has the usual Legendre polynomial ( $P_L$ ) angular dependence, but the difference in energies of the two states is shown to have associated Legendre polynomial ( $P_L^M$  with  $M = 2$ ) angular dependence. Procedures for including spin orbit coupling are included, and the extension to interactions of  $\Delta$ - and  $\Phi$ -state molecules is discussed. Values of the spherical part of the  $C_6$  coefficients for the interaction of NO with He, Ne, Ar, Kr, Xe, H, Li, Na, K, Rb, Cs,  $\text{H}_2$ ,  $\text{N}_2$ ,  $\text{O}_2$ , CO,  $\text{CO}_2$ , and NO are obtained from frequency-dependent polarizability data using Padé approximants. In addition, estimates of all the induction and angle-dependent parts of  $C_6$  are given for the NO-atom interactions.

## I. INTRODUCTION

When a diatomic molecule in  $\Pi$  electronic state interacts with an  $S$ -state atom, the interaction breaks the degeneracy of the  $\Pi$  state and two potential energy surfaces arise, one for which the electronic wavefunction is symmetric under reflection in the triatomic plane and one for which it is antisymmetric. In connection with our calculation of these two surfaces for the Ar-NO system<sup>1</sup> using the electron gas model, we became interested in also determining the van der Waals potentials for such systems. This paper presents the results of our study.

In the next section we derive the formula for the general second order van der Waals  $C_n$  coefficient for the nonrelativistic interaction of a  $\Pi$  state diatomic with an  $S$ -state atom using the notation of our recent paper on those interactions for  $\Sigma$ -state molecules.<sup>2</sup> Two surfaces are obtained. Others<sup>3,4</sup> have combined these two surfaces by introducing dependence on an azimuthal angle; however, when one does that he must remember that the additional coordinate is an *electronic* coordinate and cannot be treated as a nuclear coordinate in collision studies. To avoid confusion, we stay strictly within the Born-Oppenheimer approximation and keep two surfaces.

In Sec. II we also look in detail at the  $C_6$  coefficient and discuss ways to estimate the parts of it. In Sec. III we apply these methods to the interactions of NO ( $X^2\Pi$ ), obtaining the spherical part of  $C_6$  from frequency-dependent polarizability data using the Padé approximant methods of Langhoff and Karplus<sup>5</sup> and estimating the angle-dependent parts of  $C_6$  from available data. Then, in Sec. IV we show how to include spin-orbit coupling and also discuss the results.

## II. THEORY

### A. Derivation of general formulas

We consider a neutral molecule A in a  $\Pi$  electronic state and a neutral  $S$ -state atom B interacting at a distance large enough that electron exchange and overlap are negligible. In this section a completely nonrelativistic, spin-free Hamiltonian is used; spin-orbit ef-

fects can be included afterward as discussed in Sec. IV. Thus, were it not for the interaction, the correct zeroth-order electronic states for the molecule, regardless of total spin  $S$ , would be denoted by  $|\Lambda, M_s\rangle = |\pm 1, M_s\rangle$ , where  $\Lambda$  is the component of electronic orbital angular momentum along the molecular axis and  $M_s$  is the component of electronic spin angular momentum  $S$  along the same axis. Since  $M_s$  is being treated as a good quantum number at present, we will suppress it and write  $|\Lambda\rangle$  for  $|\Lambda, M_s\rangle$ . Now, when the atom is present, the only symmetry remaining, in general, is reflection in the plane of the three atoms, so that the degeneracy of  $|1\rangle$  and  $|-1\rangle$  is removed. If the  $x$  axis is kept perpendicular to the triatomic plane (Fig. 1), the proper zeroth-order molecular wavefunctions  $|\sigma\rangle$  are those which have definite parity  $\sigma$  under the operation  $\sigma$  which reflects  $x$  into  $-x$  (but leaves spin space alone<sup>6</sup>); that is,

$$\sigma|\sigma\rangle = (-1)^\sigma|\sigma\rangle, \quad (1)$$

where  $\sigma = 0$  and  $1$  give the even (+) and odd (-) states, respectively. However, as we have discussed elsewhere,<sup>6</sup> one has

$$\sigma|\Lambda\rangle = (-1)^{\Lambda}|\Lambda\rangle, \quad (2)$$

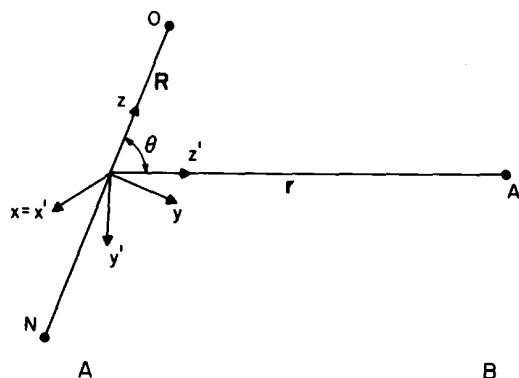


FIG. 1. Coordinate axes systems used for the interaction of a  $\Pi$ -state molecule A (in this case NO) with an  $S$ -state atom B (such as Ar). The  $x$  axis of both systems is perpendicular to the plane of the three atoms.

where  $s_A$  is a natural parity dependent on phase conventions. (For our NO example,  $s_A = 0$ .) Similarly, if  $|0\rangle$  is the ground (S) state wavefunction of atom B, it will automatically have some parity  $s_B$  under  $\sigma$ ,

$$\sigma|0\rangle = (-1)^{s_B}|0\rangle. \quad (3)$$

(It happens that  $s_B = 0$  for all the atoms used as examples in this paper.) With projection techniques one easily shows that the proper products to take as the two zeroth-order solutions of the triatomic problem are

$$|\sigma, 0\rangle = |\sigma\rangle|0\rangle = 2^{-1/2} [ |1\rangle + (-1)^{s_A+s_B+\sigma} | -1\rangle ] |0\rangle. \quad (4)$$

The long range potential is obtained by solving the electronic Schrödinger equation in the usual perturbative fashion.<sup>7</sup> The Born-Oppenheimer electronic Hamiltonian is written in the form,

$$H_\theta = H_A + H_B + V, \quad (5)$$

where  $H_A$  and  $H_B$  are the electronic Hamiltonians of molecule A and atom B, and  $V$  is the electrostatic interaction. Because atom B has no permanent multipole moments, the first order interaction energy vanishes at large distances,

$$E^{(1)} = \langle 0, \sigma | V | \sigma, 0 \rangle = 0. \quad (6)$$

The second order energy can be written, in general, in terms of a Green's function as

$$E^{(2)} = - \langle 0, \sigma | (V - E^{(1)}) [H_A + H_B - E_0(A) - E_0(B)]^{-1} \times (V - E^{(1)}) | \sigma, 0 \rangle. \quad (7)$$

In evaluating this, one is free to use any spectral representation of the Green's function he wishes. For convenience we choose to use the complete set of functions  $|\nu, n\rangle = |\nu\rangle|n\rangle$ , where  $|\nu\rangle$  and  $|n\rangle$  are the eigenfunctions of A and B, respectively, which have definite  $\Lambda$  and  $M_L(B)$  rather than definite reflection parity  $\sigma$ . Then, because of the symmetry of B, Eq. (7) becomes

$$E^{(2)} = - \sum_\nu \sum_n \frac{\langle 0, \sigma | V | \nu, n \rangle \langle \nu, n | V | \sigma, 0 \rangle}{\epsilon_\nu + \epsilon_n}, \quad (8)$$

where  $\epsilon_\nu = E_\nu(A) - E_0(A)$ , etc., and the prime implies omission of the  $n=0$  term. However, the  $\nu = |\pm 1\rangle$  induction terms are included.

When the multipole expansion for  $V$  is substituted into Eq. (8),  $E^{(2)}$  takes on the usual van der Waals form,

$$E^{(2)} = - \sum_{k=6} \gamma^{-k} C_k, \quad (9)$$

where  $\gamma$  is the distance from the center of mass of the nuclei of A to the nucleus of B, and in the notation of our recent work<sup>2</sup> on  $\Sigma$ -state interactions,  $C_k$  is given by

$$C_k = \sum_{j=3}^{k-3} \Delta_{j, k-j}, \quad (10)$$

where

$$\Delta_{j, j'} = \frac{1}{2} \sum_{l=1}^{j-2} \sum_m F(j, l, m) F(j', j' - j + l, -m) (-1)^m \times \sum_\nu \sum_n \frac{\langle \sigma | Q_l^m(A) | \nu \rangle \langle \nu | Q_{j'-j+l}^m(A) | \sigma \rangle}{\epsilon_n(\epsilon_\nu + \epsilon_n)} \times f_{0n}(j-1-l, j-1-l, B). \quad (11)$$

Here  $F(j, l, m)$  is a known coefficient,<sup>2,7,8</sup> the  $f_{0n}$  are the usual<sup>9</sup>  $2^{j-1-l}$ -pole oscillator strengths of atom B, and the  $Q_l^m(A)$  are the multipole moment operators of A (in atomic units),

$$Q_l^m(A) = [4\pi/(2l+1)]^{1/2} \sum_{i \in A} Z_i r_{iA}^l Y_l^m(\theta_i, \phi_i). \quad (12)$$

The sum in Eq. (12) is over all nuclei and electrons belonging to molecule A with coordinates measured from the center of mass of the nuclei of A and the  $z'$  axis taken to point along  $\mathbf{r}$  as in Fig. 1.

To simplify evaluation of the matrix elements in Eq. (11) we transform from the present coordinates (the primed set in Fig. 1) to a new set (unprimed in Fig. 1) in which the  $z$  axis points along the molecular axis  $\mathbf{R}$ . In doing so, the  $x$  axis is kept perpendicular to the plane of the three atoms so that reflection in the triatomic plane will be the same ( $x \rightarrow -x$ ) in both systems. To achieve this rotation through angle  $\theta$  about  $x$  using Euler angles, we rotate the axes by  $\alpha = 3\pi/2$  around  $z'$ , then by  $\beta = \theta$  around the resulting  $y''$  axis, and then by  $\gamma = \pi/2$  about the new  $z$  axis. The effect of this rotation on the multipole moment operators is

$$Q_l^m(\hat{r} = \hat{z}) = \sum_{\mu=-l}^l D_{\mu m}^l(3\pi/2, \theta, \pi/2) Q_l^\mu(\hat{R} = \hat{z}), \quad (13)$$

where the Wigner  $D$  functions are the representations of the rotation group.<sup>10,11</sup> This gives

$$\Delta_{j, j'} = \frac{1}{2} \sum_{l=1}^{j-2} \sum_m F(j, l, m) F(j', j' - j + l, -m) (-1)^m \sum_\mu \sum_{\mu'} D_{\mu m}^l D_{\mu' -j+l}^{j'-j+l} \sum_\nu \sum_n \frac{\langle \sigma | Q_l^\mu | \nu \rangle \langle \nu | Q_{j'-j+l}^{\mu'} | \sigma \rangle}{\epsilon_n(\epsilon_\nu + \epsilon_n)} f_{0n}(j-1-l, j-1-l), \quad (14)$$

where we have suppressed the arguments of the  $D$  functions and also the A and B labels where  $\nu$  and  $n$  make them clear. Coupling the two Wigner  $D$  functions together via the Clebsch-Gordan theorem<sup>10,12</sup> gives

$$\Delta_{j, j'} = \frac{1}{2} \sum_{l=1}^{j-2} \sum_L \alpha(L, l, j, j') \sum_\mu \sum_{\mu'} C(l, j' - j + l, L; \mu, \mu', \mu + \mu') D_{\mu + \mu', 0}^L \sum_\nu \sum_n \frac{\langle \sigma | Q_l^\mu | \nu \rangle \langle \nu | Q_{j'-j+l}^{\mu'} | \sigma \rangle}{\epsilon_n(\epsilon_\nu + \epsilon_n)} f_{0n}(j-1-l, j-1-l), \quad (15)$$

where<sup>2</sup>

$$\alpha(L, l, j, j') = \sum_m (-1)^m F(j, l, m) F(j', j' - j + l, -m) C(l, j' - j + l; L, m, -m, 0), \quad (16)$$

$$= \frac{(-1)^{j'-l+1+L}}{(2j-2l-2)!} \left[ \frac{(2j-1)!(2j'-1)!}{(2l)!(2j'-2j+2l)!} \right]^{1/2} C(j-1, j'-1, L; 000) W(j-l-1, l, j'-1, L; j-1, j'-j+l), \quad (17)$$

and  $W$  is a Racah coefficient.<sup>13</sup> For those values of the parameters for which  $\alpha$  is nonzero, it reduces to

$$\alpha(L, l, j, j') = \frac{(-1)^{(j-j'+L)/2-1} (j+j'-L-2)! \left(\frac{j+j'+L-2}{2}\right)!}{(2j-2l-2)! \left(\frac{j+j'-L-2}{2}\right)! \left(\frac{j-j'+L}{2}\right)! \left(\frac{j'-j+L}{2}\right)!} \left[ \frac{(2L+1)(j-j'+L)!(j'-j+L)!}{(j'-j+2l+1+L)!(j'-j+2l-L)!} \right]^{1/2}. \quad (18)$$

Use of the definition [Eq. (4)] for  $|\sigma\rangle$ , the  $m$ -type selection rule, and the fact that state  $|\nu\rangle$  has a well-defined angular momentum projection  $\Lambda_\nu$  along the molecular axis allows the sums over  $\mu$  and  $\mu'$  in Eq. (15) to be done and gives

$$\begin{aligned} \Delta_{jj'} = & \frac{1}{4} \sum_{l=1}^{j-2} \sum_L \alpha(L, l, j, j') \sum_{\nu} \sum_{\pi} \frac{f_{0\pi}(j-1-l, j-1-l)}{\epsilon_n(\epsilon_\nu + \epsilon_\pi)} [D_{0,0}^L C(l, j'-j+l, L; 1-\Lambda_\nu, \Lambda_\nu-1, 0) \langle 1 | Q_i^{1-\Lambda_\nu} | \nu \rangle \langle \nu | Q_{j',-j+l}^{\Lambda_\nu-1} | 1 \rangle \\ & + D_{0,0}^L C(l, j'-j+l, L; -1-\Lambda_\nu, \Lambda_\nu+1, 0) \langle -1 | Q_i^{1-\Lambda_\nu} | \nu \rangle \langle \nu | Q_{j',-j+l}^{\Lambda_\nu+1} | -1 \rangle + (-1)^{s_A+s_B+s_\sigma} D_{2,0}^L C(l, j'-j+l, L; 1-\Lambda_\nu, \Lambda_\nu \\ & + 1, 2) \langle 1 | Q_i^{1-\Lambda_\nu} | \nu \rangle \langle \nu | Q_{j',-j+l}^{\Lambda_\nu+1} | -1 \rangle + (-1)^{s_A+s_B+s_\sigma} D_{-2,0}^L C(l, j'-j+l, L; -1-\Lambda_\nu, \Lambda_\nu-1, -2) \langle -1 | Q_i^{1-\Lambda_\nu} | \nu \rangle \\ & \times \langle \nu | Q_{j',-j+l}^{\Lambda_\nu-1} | 1 \rangle ]. \end{aligned} \quad (19)$$

The  $D$  functions here reduce<sup>10,14</sup> to spherical harmonics or to associated Legendre polynomials,<sup>15</sup>

$$D_{M,0}^L(3\pi/2, \theta, \pi/2) = [4\pi/(2L+1)]^{1/2} Y_L^M(-\theta, -\pi/2), \quad (20)$$

$$= \left[ \frac{(L-M)!}{(L+M)!} \right]^{1/2} P_L^M(\cos\theta) e^{iM\pi/2}. \quad (21)$$

Using this and the relation

$$Y_L^{-M} = (-1)^M Y_L^M, \quad (22)$$

to avoid dealing with  $P_L^{-2}$ , we have

$$\begin{aligned} \Delta_{jj'} = & \frac{1}{4} \sum_{l=1}^{j-2} \sum_L \alpha(L, l, j, j') \sum_{\nu} \sum_{\pi} \frac{f_{0\pi}(j-1-l, j-1-l)}{\epsilon_n(\epsilon_\nu + \epsilon_\pi)} \{ P_L^0(\cos\theta) [C(l, j'-j+l, L; 1-\Lambda_\nu, \Lambda_\nu-1, 0) \langle 1 | Q_i^{1-\Lambda_\nu} | \nu \rangle \\ & \times \langle \nu | Q_{j',-j+l}^{\Lambda_\nu-1} | 1 \rangle + C(l, j'-j+l, L; -1-\Lambda_\nu, \Lambda_\nu+1, 0) \langle -1 | Q_i^{1-\Lambda_\nu} | \nu \rangle \langle \nu | Q_{j',-j+l}^{\Lambda_\nu+1} | -1 \rangle ] - (-1)^{s_A+s_B+s_\sigma} \left( \frac{(L-2)!}{(L+2)!} \right)^{1/2} \\ & \times P_L^2(\cos\theta) [C(l, j'-j+l, L; 1-\Lambda_\nu, \Lambda_\nu+1, 2) \langle 1 | Q_i^{1-\Lambda_\nu} | \nu \rangle \langle \nu | Q_{j',-j+l}^{\Lambda_\nu+1} | -1 \rangle + C(l, j'-j+l, L; -1-\Lambda_\nu, \Lambda_\nu-1, -2) \\ & \times \langle -1 | Q_i^{1-\Lambda_\nu} | \nu \rangle \langle \nu | Q_{j',-j+l}^{\Lambda_\nu-1} | 1 \rangle ] \}. \end{aligned} \quad (23)$$

Thus, it is seen that in addition to the ordinary Legendre polynomial  $P_L^0$  angle-dependent terms which are essentially the same as those obtained for the interactions of  $\Sigma$ -state molecules,<sup>2</sup> the natural expression for the  $C_n$  for  $\Pi$ -state molecules also involves the associated Legendre polynomials  $P_L^2$ . Since the  $P_L^0 = P_L$  form a complete set, one could express the  $P_L^2$  as linear combinations of the  $P_L$ , but, as we will show in a future paper<sup>1</sup> on collisions in these systems, it is convenient to keep the  $P_L^2$  in there. Also, the fact that  $P_L^2 = 0$  when  $\theta = 0$  or  $\pi$  makes it clear that the difference in energies of the two states with different  $\sigma$  vanishes, as it should, when the triatomic system is linear.

From Eq. (23) one could generate explicit expressions for any  $C_n$  coefficient desired as we recently did in getting coefficients through  $C_6$  for  $\Sigma$ -state molecules.<sup>2</sup> However, there is presently not enough information available for most  $\Pi$ -state molecules to calculate anything past  $C_6$  with any reliability; hence, we only consider  $C_6$  in the next subsection. Before doing so, we note in passing that the procedure just presented can be extended very simply to treat van der Waals inter-

actions of molecules in  $\Delta$ ,  $\Phi$ , etc. ( $\Lambda = 2, 3$ , etc.) states. Everything goes through as before except that in Eq. (4) one has

$$|\sigma\rangle = 2^{-1/2} [ |\Lambda\rangle + (-1)^{s_A+s_B+s_\sigma} |-\Lambda\rangle ]. \quad (24)$$

Equation (15) is obtained as at present, but Eqs. (19) and (23) are generalized, and the angle dependence obtained involves the  $P_L^{|\Lambda|}$  in addition to the usual  $P_L^0$ .

## B. The $C_6$ coefficient

Let us now construct simpler explicit formulas for  $C_6$ . We start from Eq. (10),

$$C_6 = \Delta_{33}, \quad (25)$$

and from Eq. (15), rather than Eq. (23), to make comparison with the usual formulas easier. Thus,  $C_6$  is given by

$$C_6 = \frac{1}{2} \sum_{L=0}^2 \alpha(L, 1, 3, 3) \sum_{\mu} \sum_{\mu'} C(1, 1, L; \mu, \mu', \mu + \mu') \times D_{\mu+\mu', 0}^L \sum_{\nu} \sum_{\pi} \frac{\langle \sigma | Q_1^{\mu'} | \nu \rangle \langle \nu | Q_1^{\mu} | \sigma \rangle}{\epsilon_n(\epsilon_\nu + \epsilon_\pi)} f_{0\pi}(1, 1). \quad (26)$$

We break this up into induction and dispersion contributions,

$$C_6 = C_6(\text{ind}) + C_6(\text{dis}), \quad (27)$$

and consider each separately.

### 1. Induction terms

The induction contributions come from the terms with  $|\nu\rangle = |1\rangle$  and  $|-1\rangle$ . Noting that  $-1 \leq \mu, \mu' \leq 1$ , one sees that all matrix elements like  $\langle -1 | Q_1^\mu | 1 \rangle$  are zero due to the  $m$ -type selection rule, and all that survive are the  $\mu = \mu' = 0$  terms, so that  $C_6(\text{ind})$  becomes

$$C_6(\text{ind}) = \frac{1}{4} \sum_{L=0}^2 \alpha(L, 1, 3, 3) C(1, 1, L; 0, 0, 0) D_{0,0}^L \alpha(B) \\ \times [ \langle 1 | Q_1^0 | 1 \rangle \langle 1 | Q_1^0 | 1 \rangle + \langle -1 | Q_1^0 | -1 \rangle \\ \times \langle -1 | Q_1^0 | -1 \rangle ], \quad (28)$$

where  $\alpha(B)$ , given by

$$\alpha(B) = \sum_n' f_{0n} \epsilon_n^{-2}, \quad (29)$$

is the usual static dipole polarizability of atom B. The matrix elements left here are all equal to the ordinary dipole moment of A, due to

$$\mu(A) = \langle 1 | Q_1^0 | 1 \rangle = (-1)^{s_A} \langle \sigma(-1) | Q_1^0 | 1 \rangle \\ = (-1)^{s_A} \langle -1 | \sigma Q_1^0 | 1 \rangle = (-1)^{s_A} \langle -1 | Q_1^0 \sigma | 1 \rangle \\ = \langle -1 | Q_1^0 | -1 \rangle. \quad (30)$$

Here  $\sigma$  only need reflect the molecular coordinates, and we have used the commutation relation<sup>6</sup>

$$\sigma Q_1^m = Q_1^{-m} \sigma. \quad (31)$$

Use of Eq. (21) and evaluation of the coefficients in Eq. (28) gives

$$C_6(\text{ind}) = C_6(0, \text{ind}) + C_6(2, \text{ind}) P_2^0(\cos\theta), \quad (32a)$$

where

$$C_6(0, \text{ind}) = C_6(2, \text{ind}) = \alpha(B) \mu^2(A), \quad (32b)$$

which is exactly the formula obtained for  $\Sigma$ -state molecules, so that nothing new is needed for this term for  $\Pi$  states.

### 2. Dispersion terms

The dispersion contribution is given by the terms in Eq. (26) for which  $|\nu\rangle \neq |\pm 1\rangle$  and  $n \neq 0$ . The matrix elements involved are

$$\langle \sigma | Q_1^\mu | \nu \rangle \langle \nu | Q_1^{\mu'} | \sigma \rangle = \frac{1}{2} \{ [ \langle 1 | Q_1^\mu | \nu \rangle \langle \nu | Q_1^{\mu'} | 1 \rangle + \langle -1 | Q_1^\mu | \nu \rangle \\ \times \langle \nu | Q_1^{\mu'} | -1 \rangle ] + (-1)^{s_A + s_B + \sigma} [ \langle 1 | Q_1^\mu | \nu \rangle \\ \times \langle \nu | Q_1^{\mu'} | -1 \rangle + \langle -1 | Q_1^\mu | \nu \rangle \langle \nu | Q_1^{\mu'} | 1 \rangle ] \}. \quad (33)$$

We assert that the first two terms here give equal contributions to the sum, and the last two do likewise. To prove this we represent  $|\nu\rangle$  by  $|\Lambda_\nu\rangle$  for clarity and use manipulations such as those in Eq. (30) to show that

$$\langle -1 | Q_1^\mu | \Lambda_\nu \rangle \langle \Lambda_\nu | Q_1^{\mu'} | -1 \rangle = \langle 1 | Q_1^{-\mu} | -\Lambda_\nu \rangle \langle -\Lambda_\nu | Q_1^{-\mu'} | 1 \rangle, \quad (34)$$

and

$$\langle -1 | Q_1^\mu | \Lambda_\nu \rangle \langle \Lambda_\nu | Q_1^{\mu'} | 1 \rangle = \langle 1 | Q_1^{-\mu} | -\Lambda_\nu \rangle \langle -\Lambda_\nu | Q_1^{-\mu'} | -1 \rangle, \quad (35)$$

where  $\sigma |\Lambda_\nu\rangle = (-1)^{\Lambda_\nu} |-\Lambda_\nu\rangle$ . Now, the  $\mu$ -type sums run symmetrically over positive and negative values,  $\alpha(L, 1, 3, 3)$  is only nonzero for even  $L$ , for which the Clebsch-Gordan coefficient is symmetric<sup>12</sup> under change of sign of  $\mu$  and  $\mu'$ , and in the present case  $D_{-\mu, -\mu', 0}^L = D_{\mu, \mu', 0}^L$ , so that we can change the signs of  $\mu$  and  $\mu'$  in the right hand sides of Eqs. (34) and (35). That proves the assertion for all states  $\nu$  for which  $\Lambda_\nu = 0$ . For any state with  $\Lambda_\nu \neq 0$ , there is always another state with the same energy and  $-\Lambda_\nu$  in the sum, so that the total contributions are equal. Furthermore, we note that the  $m$ -type selection rule is only satisfied if  $\mu' = -\mu$  in the first term and  $\mu' = 2 - \mu$  in the third term of Eq. (33). Using these simplifications, we can write

$$C_6(\text{dis}) = C_6(0, \text{dis}) + C_6(2, \text{dis}) P_2^0(\cos\theta) + (-1)^{\sigma} D_6 P_2^2(\cos\theta), \quad (36)$$

where

$$C_6(L, \text{dis}) = \frac{1}{2} \alpha(L, 1, 3, 3) \sum_{\mu} C(1, 1, L; \mu, -\mu, 0) \\ \times \sum_{\nu}' \sum_n' \frac{\langle 1 | Q_1^\mu | \nu \rangle \langle \nu | Q_1^{-\mu} | 1 \rangle}{\epsilon_n(\epsilon_\nu + \epsilon_n)} f_{0n}(1, 1), \quad (37)$$

and

$$D_6 = \frac{1}{2} (-1)^{s_A + s_B + 1} \alpha(2, 1, 3, 3) \sum_{\mu} C(1, 1, 2; \mu, 2 - \mu, 2) (41)^{-1/2} \\ \times \sum_{\nu}' \sum_n' \frac{\langle 1 | Q_1^\mu | \nu \rangle \langle \nu | Q_1^{2-\mu} | -1 \rangle}{\epsilon_n(\epsilon_\nu + \epsilon_n)} f_{0n}(1, 1). \quad (38)$$

In the  $C_6(L, \text{dis})$  we note that

$$\langle 1 | Q_1^\mu | \nu \rangle \langle \nu | Q_1^{-\mu} | 1 \rangle = (-1)^\mu | \langle \nu | Q_1^{-\mu} | 1 \rangle |^2, \quad (39)$$

and define  $\mu$ -dependent oscillator strengths<sup>2</sup> by

$$f_{0\nu}^{-\mu}(1, 1) = 2\epsilon_\nu | \langle \nu | Q_1^{-\mu} | 1 \rangle |^2. \quad (40)$$

With this it is clear that the  $C_6(L, \text{dis})$ , in which  $\Lambda = 1$  is conserved, are exactly the well-known terms that appear in  $\Sigma$ -state interactions. Evaluating the coefficients in Eq. (37) gives the usual formulas

$$C_6(0, \text{dis}) = \frac{3}{2} \sum_{\nu, n}'' \frac{\bar{f}_{0\nu} f_{0n}}{\epsilon_n \epsilon_\nu (\epsilon_n + \epsilon_\nu)}, \quad (41)$$

and

$$C_6(2, \text{dis}) = \frac{1}{2} \sum_{\nu, n}'' \frac{f_{0n}}{\epsilon_n \epsilon_\nu (\epsilon_n + \epsilon_\nu)} (f_{0\nu}^0 - \frac{1}{2} f_{0\nu}^1 - \frac{1}{2} f_{0\nu}^{-1}), \quad (42)$$

where

$$\bar{f}_{0\nu} = \frac{1}{3} \sum_{\mu} f_{0\nu}^{-\mu},$$

and for the atom  $f_{0n} = \bar{f}_{0n}$ .

To simplify the equation for the new coefficient,  $D_6$ , we note that the operators  $Q_1^\mu$  and  $Q_1^{2-\mu}$  are both nonzero only if  $-1 \leq \mu \leq 1$  and  $-1 \leq 2 - \mu \leq 1$  which is true only for  $\mu = 1$ . This means also that the only states  $\nu$  that contribute to Eq. (38) are those with  $\Lambda_\nu = 0$ ; i. e.,  $\Sigma$  states. Using that, reflection symmetry, and Eqs. (39) and (40), one has

$$\langle \nu | Q_1^\dagger | -1 \rangle = (-1)^{s_A + s_\nu} \langle \nu | Q_1^{-1} | 1 \rangle, \quad (43)$$

and

$$D_6 = \frac{1}{8} (4!)^{-1/2} (-1)^{s_B} \alpha(2, 1, 3, 3) C(1, 1, 2; 1, 1, 2) \\ \times \sum_{\nu, n}'' (-1)^{s_\nu} f_{0\nu}^{-1}(1, 1) f_{0n}(1, 1) / \epsilon_n \epsilon_\nu (\epsilon_n + \epsilon_\nu), \quad (44)$$

or

$$D_6 = \frac{1}{8} \sum_{\nu, n}'' \frac{(-1)^{s_\nu + s_B} f_{0\nu}^{-1}(1, 1) f_{0n}(1, 1)}{\epsilon_n \epsilon_\nu (\epsilon_n + \epsilon_\nu)}. \quad (45)$$

### C. Evaluation of $C_6$

Now let us consider ways to calculate or estimate the values of the exact formulas [Eqs. (32), (41), (42), and (45)]. Accurate theoretical or experimental values of  $\alpha(B)$  and  $\mu(A)$  are often available, so that the  $C_6(L, \text{ind})$  are easily obtained for many systems.  $C_6(0, \text{dis})$  can be obtained accurately from experimental frequency-dependent polarizability data using Padé approximants,<sup>5, 16</sup> Eq. (41), and

$$C_6(0, \text{dis}) = 3(2\pi)^{-1} \int_{-\infty}^{\infty} \bar{\alpha}_A(iy) \alpha_B(iy) dy, \quad (46)$$

where  $\bar{\alpha}_A(iy)$  is the average polarizability of molecule A at the imaginary frequency  $iy$ . If the frequency dependence of the polarizability anisotropy is known, then  $C_6(2, \text{dis})$  can be obtained the same way.<sup>17</sup> However, if the polarizability anisotropy  $\kappa$  of A is known at only one frequency, then, as we have shown elsewhere,<sup>2</sup> reasonably good bounds on  $C_6(2, \text{dis})$  can often still be obtained from

$$C_6(2, \text{dis}) = a_6 C_6(0, \text{dis}), \quad (47)$$

where

$$(\alpha_{\parallel}^{3/4} - \alpha_{\perp}^{3/4}) / (\alpha_{\parallel}^{3/4} + 2\alpha_{\perp}^{3/4}) \lesssim a_6 \lesssim \kappa = (\alpha_{\parallel} - \alpha_{\perp}) / (\alpha_{\parallel} + 2\alpha_{\perp}), \quad (48)$$

and  $\alpha_{\parallel}$  and  $\alpha_{\perp}$  are the parallel and perpendicular polarizabilities of A, respectively.

Evaluation of Eq. (45) to get  $D_6$  appears to be much more difficult. One might think of relating it to the similar parts of  $C_6(2, \text{dis})$  but, in contrast to  $\Sigma$  states,  $f_{0\nu}^1 \neq f_{0\nu}^{-1}$  in Eq. (42), and it should also be noted that the contributions of the excited  $\Sigma^+$  and  $\Sigma^-$  states in Eq. (45) have opposite signs. About all that can be said at the moment is that  $D_6$  should be small compared to  $C_6(0, \text{dis})$ . The only experiments<sup>3, 4</sup> that we know of, that do not involve the  $\sigma = 0$  and  $\sigma = 1$  states in equal numbers and give averages in which all information about  $D_6$  cancels out, require detailed analysis of collisions and will be discussed in a future paper.<sup>1</sup> It is now possible (but not easy) to obtain  $D_6$  from accurate *ab initio* calculations, and such calculations are to be encouraged. The equivalent calculations for interactions of  $P$ -state atoms have been carried out for some systems, and in the next section we use atomic results to get a rough estimate of  $D_6$  for NO interactions.

### III. CALCULATIONS AND RESULTS

The van der Waals coefficients of the previous section are functions of the internuclear distance of the

molecule. However, since we use experimental data in the present calculations, the results represent an average over the ground state vibration of the molecule.

Using the experimental dipole moment<sup>18</sup> of NO,  $\mu(\text{NO}) = -0.158 \text{ D} = -0.062 \text{ a. u.}$  and the sum rules  $S(-2) = \alpha(B)$  of Langhoff and Karplus,<sup>5, 19</sup> we obtain the values of  $C_6(L, \text{ind})$  shown in Table II.

The frequency-dependent polarizability was obtained from refractive index data using the Lorenz-Lorentz equation,<sup>20</sup>

$$\bar{\alpha}(\omega) = \frac{3}{4\pi n} \frac{(\eta^2 - 1)}{(\eta^2 + 2)}, \quad (49)$$

where  $\eta$  is the refractive index at frequency  $\omega$ , and  $n$  is the number density of molecules. The Benedict-Webb-Rubin equation of state<sup>21</sup> for NO gives  $3/4\pi n = 60\,035 \text{ a}_0^3$  at STP. Refractive index values were found at 22 visible and ultraviolet wavelengths ranging from 224.7 to 670.9 nm.<sup>22, 23</sup> No infrared data were found; however, only the electronic (essentially the uv) part of  $\bar{\alpha}(\omega)$  goes into Eq. (46), and NO has a small dipole moment, so that it is clear from our work<sup>24</sup> on CO that the ir spectrum of NO contributes negligibly to the available  $\bar{\alpha}(\omega)$ . A rough value of the zero frequency polarizability of NO,  $\bar{\alpha}(0) = 11.70 \pm 0.27 \text{ a}_0^3$ , was obtained from available dielectric constant data<sup>25</sup> and the Clausius-Mosotti equation<sup>20</sup>; it is consistent with the value of  $\bar{\alpha}(0) = S(-2)$  obtained below but not accurate enough to add any information.

Because there is much less data available in this case than there was for CO<sup>24</sup> or CO<sub>2</sub>,<sup>16</sup> nothing could be gained by using the finite linewidth formulas employed there, and the Langhoff-Karplus<sup>5</sup> procedure was followed directly. Briefly summarized, the frequency-dependent polarizability,

$$\bar{\alpha}(\omega) = \sum_{\nu} \frac{f_{0\nu}}{\epsilon_{\nu}^2 - \omega^2}, \quad (50)$$

is expanded in the Cauchy series,

$$\bar{\alpha}(\omega) = \sum_k S(-2k-2) \omega^{2k}, \quad (51)$$

and the sum rules  $S(j)$  are determined by fitting the experimental data. Then, these sum rules are used to construct upper and lower bounding Padé approximants to  $\bar{\alpha}(\omega)$  which can be put in the form of Eq. (50) with a finite sum, and used in Eq. (46) to obtain bounds to  $C_6(0, \text{dis})$ . In fitting the limited available data with Eq. (51), five coefficients were kept and determined by an iterative procedure in which the first three coefficients were obtained from a linear least-squares method and  $S(-8)$  and  $S(-10)$  were determined by a nonlinear method<sup>26</sup> which assured satisfaction of the Stieltjes constraints.<sup>5</sup> The resulting sum rules, which fit the data with a standard deviation of  $0.0068 \text{ a}_0^3$ , are in Table I. The  $S(0)$  in this table was obtained from the Reiche-Thomas-Kuhn<sup>9</sup> theorem. To obtain reasonable uncertainty limits for the  $S(j)$ , which reflect the effects of omitting the higher terms in Eq. (51),  $S(-10)$  (which is not needed in the  $[2, 1]$  Padé approximants used) was varied within the range allowed by the Stieltjes constraints and the induced fluctuations in the  $S(j)$  were

TABLE I. Oscillator strength sums for NO. Hartree atomic units.

$j$	$S(j)$
0	15.0000
-2	11.518 ± 0.013
-4	39.05 ± 0.22
-6	246 ± 12
-8	(4.19 ± 0.10) × 10 <sup>3</sup>
-10	(1.0 ± 0.1) × 10 <sup>5</sup>

found. Because of the limited data available, these  $S(j)$  are considerably less accurate than those obtained recently for other molecules.<sup>16,24</sup>

The  $C_6(0, \text{dis})$  for the interaction of NO with a number of partners (using the sum rules of Refs. 5, 16, and 24) are in Table II. The values given are the means of the best Padé bounds, but the error bounds have been extended to include the effects of the uncertainties in the sum rules.

Using the experimental value<sup>27</sup> of the polarizability anisotropy of NO,  $\kappa = 0.161$ , and Eq. (48), we obtain

$$a_6 = 0.141 \pm 0.021, \quad (52)$$

and use this and Eq. (47) to generate the  $C_6(2, \text{dis})$  shown in Table II.

To get a rough estimate of  $D_6$  we note that the contribution to  $s_B$  in Eq. (45) of closed shells is always zero, and all the atoms in Table II are either closed shell or have one  $s$ -type electron outside a closed shell, so that  $s_B = 0$ . Also, since all the low-lying excited states<sup>28</sup> of NO that occur in Eq. (45) are  $\Sigma^+$  states ( $s_v = 0$ ), we expect  $D_6$  to be positive and from Eq. (36)  $C_6$  for the  $+$  ( $\sigma = 0$ ) state to be larger than that of the  $-$  state. This is consistent with the observation that the electronic structure of NO is basically that of closed-shell  $N_2(1\Sigma_g^+)$  plus one extra electron in a  $\pi$  orbital. The  $-$  state corresponds to a  $\pi_x$  orbital (see Fig. 1), and the

$+$  state to a  $\pi_y$  orbital which sticks out in the plane of the atom and is more strongly polarized by it. This interpretation in terms of orbital directions also predicts correctly the relative values of all the  $\Sigma$ - and  $\Pi$ -state polarizabilities calculated for  $P$ -state atoms by Stevens and Billingsley.<sup>29</sup> Assuming that NO is like the O atom, that is, that the ratio of the two  $C_6$  coefficients in the direction perpendicular to the NO axis is equal to the ratio of O polarizabilities,<sup>29</sup> we have

$$\frac{C_6^-(\text{dis}, \theta = \pi/2)}{C_6^+(\text{dis}, \theta = \pi/2)} \approx \frac{\alpha_0(\Pi)}{\alpha_0(\Sigma)} = \frac{0.66}{0.74}. \quad (53)$$

Letting  $D_6 = \delta C_6(0, \text{dis})$  and using Eq. (36) we have

$$\frac{1 - \frac{1}{2}a_6 - 3\delta}{1 - \frac{1}{2}a_6 + 3\delta} = \frac{0.66}{0.74}, \quad (54)$$

and with Eq. (52) we have

$$\delta = 0.018 \pm 0.010, \quad (55)$$

which was used to generate the last column of Table II. The uncertainty in Eq. (55) is a guesstimate based on the following: the polarizability of NO is nearer that of C than O; use of the ratio<sup>29</sup> for C would give  $\delta = 0.035$ . But NO has more electrons than O, so that changing the direction of one electron should have a proportionately smaller effect and give a smaller  $\delta$  than that from O. This uncertainty makes it clear that the present rough estimate of  $D_6$  is mostly an illustrative example calculation.

## IV. CONCLUSION

### A. Spin-orbit effects

In the preceding sections we have assumed a completely nonrelativistic model with spin and orbital angular momentum completely uncoupled. For  $^1\Pi$  molecules interacting with  $^1S$  atoms this is adequate. However, NO is a  $^2\Pi$ -state molecule with spin-orbit splitting constant<sup>28</sup>  $\bar{A} = 124.2 \text{ cm}^{-1} = 5.66 \times 10^{-4} \text{ a.u.}$  For the interaction of NO with the  $^1S$  atoms in Table II, the  $r$ -dependent relativistic corrections are negligible,<sup>30</sup> so

TABLE II. Contributions to the van der Waals  $C_6$  coefficients for the interaction of NO( $^2\Pi$ ) with several partners. The angle-dependent terms are omitted for the molecular partners as the formulas in the paper are not appropriate for them. Hartree atomic units ( $e^2 a_0^5$ ).

Partner	$C_6(0, \text{ind})$ $= C_6(2, \text{ind})$	$C_6(0, \text{dis})$	$C_6(2, \text{dis})$	$C_6(0, \text{tot})$	$C_6(2, \text{tot})$	$D_6$
He	0.00535	9.8 ± 1.3	1.41 ± 0.39	9.8 ± 1.3	1.41 ± 0.39	0.18 ± 0.11
Ne	0.0103	21.0 ± 3.6	3.00 ± 0.95	21.0 ± 3.6	3.01 ± 0.95	0.38 ± 0.25
Ar	0.0429	69 ± 10	9.9 ± 2.9	69 ± 10	9.9 ± 2.9	1.24 ± 0.79
Kr	0.0647	98 ± 15	14.0 ± 4.3	98 ± 15	14.1 ± 4.3	1.8 ± 1.1
Xe	0.106	170 ± 31	24.3 ± 8.0	170 ± 31	24.4 ± 8.0	3.1 ± 2.0
H	0.0174	20.2 ± 1.4	2.89 ± 0.63	20.2 ± 1.4	2.91 ± 0.63	0.36 ± 0.21
Li	0.633	177.8 ± 4.6	25.4 ± 4.4	178.4 ± 4.6	26.1 ± 4.4	3.2 ± 1.9
Na	0.647	217 ± 16	31.1 ± 6.9	218 ± 16	31.7 ± 6.9	3.9 ± 2.3
K	1.11	321 ± 25	46 ± 10	322 ± 25	47 ± 10	5.8 ± 3.5
Rb	1.22	364 ± 30	52 ± 12	365 ± 30	53 ± 12	6.6 ± 3.9
Cs	1.38	314 ± 16	44.8 ± 8.9	315 ± 16	46.2 ± 8.9	5.7 ± 3.3
H <sub>2</sub>	...	28.2 ± 2.4	...	...	...	...
N <sub>2</sub>	...	71.1 ± 9.3	...	...	...	...
O <sub>2</sub>	...	55.2 ± 4.9	...	...	...	...
CO <sub>2</sub>	...	113 ± 14	...	...	...	...
CO	...	78 ± 12	...	...	...	...
NO	...	69 ± 13	...	...	...	...

that all that need be added is the spin-orbit splitting of the NO. This can be done by using the phenomenological Hamiltonian,

$$H = H_0 + \bar{A}L_z(A)S_z(A), \quad (56)$$

instead of Eq. (5). The two terms in this  $H$  are not simultaneously diagonal, so that if we use the eigenfunctions of  $H_0$  obtained in the previous sections (denoted by  $|\sigma, 0\rangle \equiv |\sigma, M_s, 0\rangle = |\pm, M_s, 0\rangle$  with eigenvalues  $E^\pm$ ) as a basis, a two by two secular equation results (only  $2 \times 2$  as  $M_s$  stays a good quantum number here) which has the simple form

$$\begin{vmatrix} E^+ - E & \bar{A}M_s \\ \bar{A}M_s & E^- - E \end{vmatrix} = 0. \quad (57)$$

This has the eigenvalues

$$E = (E^+ + E^-)/2 \pm \{[(E^+ - E^-)/2]^2 + (\bar{A}/2)^2\}^{1/2}. \quad (58)$$

For small  $r$  with  $\theta$  not near 0 or  $\pi$  the  $E^+ - E^-$  term dominates and the present basis is appropriate. For large  $r$  or  $\theta$  near 0 or  $\pi$  and the LS coupling dominates and the appropriate basis is the set  $|\Lambda, M_s, 0\rangle$ , which describes the  ${}^2\Pi_{3/2}$  and  ${}^2\Pi_{1/2}$  states. In the present examples, the spin-orbit coupling dominates in most of the van der Waals region, and the appropriate potentials are easily generated using Eq. (58).

The above approach can also be used for the interaction of NO( ${}^2\Pi$ ) with the  ${}^2S$ -state atoms of Table II unless very high accuracy is desired in which case one would need to include the small ( $\lesssim 0.05 \text{ cm}^{-1}$ ) magnetic dipole-dipole interaction.<sup>30</sup>

## B. Discussion

In this paper we have rigorously shown that the van der Waals potential between a  $\Pi$ -state molecule and an  $S$ -state atom does have the associated Legendre polynomial dependence which others have assumed<sup>3</sup> or argued<sup>4</sup> that it should have. The accuracy of the present  $C_6(0, \text{dis})$  for NO interactions is the best obtainable using the present data; other methods<sup>17</sup> would give the same results from the same data. However, it might be possible to obtain improved accuracy by using the method of Starkschall and Gordon<sup>31</sup> which allows one to also use other types of data. A better determination of the new  $D_6$  coefficients than the present rough estimate is likely to be difficult experimentally and best accomplished by accurate *ab initio* calculations.

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