

CALCULATION OF THE MULTIPOLE POLARIZABILITIES AND VAN DER WAALS  
CONSTANTS FOR NOBLE GAS ATOMS

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Submitted February 21, 1972

Zh. Eksp. Teor. Fiz. 63, 889-898 (September, 1972)

The dipole dynamic polarizabilities of Ne, Ar, Kr and Xe atoms are calculated within the framework of the Hartree-Fock method and by taking into account correlations in the random-phase-with-exchange approximation. The importance of allowance for many-electron correlations is shown. The quadrupole polarizability and the constants  $C_6$  and  $C_8$ , which characterize the interaction of atoms of noble gases at large distances, are calculated in similar fashion. The concept of "monopole" polarizability is introduced, in terms of which the polarization potential at small distances from the nucleus and the deviation of the ionization potentials of the inner shells from those obtained in the Hartree-Fock approximation can be expressed.

1. In calculations of the dipole dynamic polarizability, one can distinguish three basic directions. The first<sup>[1,2]</sup> uses the sum rule for the oscillator strengths. The second direction, developed in<sup>[3,4]</sup>, uses the variational principle. And, finally, the third direction<sup>[5-7]</sup> uses the methods of many-body theory.<sup>1)</sup> Up to the present time, calculations of the dipole dynamic polarizability are known only for comparatively light atoms. We have obtained the dipole dynamic polarizability for atoms of the noble gases Ne, Ar, Kr and Xe. The quadrupole dynamic polarizability has been calculated for Ar. The concept of "monopole" polarizability has been introduced. (This quantity appears in the study of the interaction of a heavy, slow, charged particle with an atom at small distances and in considerations of some other phenomena.)

The calculations were made by means of the Hartree-Fock method with account of many-electron correlations—in the random phase approximation with exchange (RPAE). In this approximation, the London constant of the interaction potential between two pairs of atoms of noble gases is calculated. Excellent agreement is obtained with the semi-empirical calculations, and with such experimental data as exist. It is shown that the effect of the many-electron correlations on the polarizability and interaction of two atoms at large distances are great.

2. The dipole dynamic polarizability is determined by the relation

$$\alpha_d(\omega) = \sum_n \frac{F_n}{\omega_n^2 - \omega^2}, \tag{1}$$

where  $F_n = 2\omega_n |\langle 0 | d | n \rangle|^2$  is the oscillator strength,  $d$  the dipole moment operator of the system and  $\omega_n = E_n - E_0$  the excitation energy. The sum over  $n$  includes summation over all discrete excited states of the sys-

tem and integration over the continuous spectrum. (The atomic units  $\hbar = m = e = 1$  are used throughout.) The oscillator strengths satisfy the sum rule

$$\sum_n F_n = N, \tag{2}$$

where  $N$  is the number of electrons in the atom.

The dipole polarizabilities in the single-electron approximation can be expressed by the diagram shown in Fig. 1. Here the continuous line with the arrows directed to the right or left corresponds to a particle or hole. The dashed line corresponds to the external field.

We introduce the spectral distribution function of the dipole excitations:

$$g(\omega) = \sum_n F_n \delta(\omega - \omega_n) = \frac{2}{\pi} \omega \text{Im} \alpha_d(\omega). \tag{3}$$

The dispersion relation connecting the real and imaginary parts of the polarizability follows directly from (3) and (1). We take it into account that the cross section  $\sigma(\omega)$  of the photoeffect is directly proportional to the spectral function  $g(\omega)$  for values of  $\omega$  that exceed the ionization threshold:

$$\sigma(\omega) = 2\pi^2 c^{-4} g(\omega). \tag{4}$$

Then

$$\text{Re} \alpha_d(\omega) = \sum_k \frac{F_k}{\omega_k^2 - \omega^2} + \frac{c}{2\pi^2} \int \frac{\sigma(\omega')}{\omega'^2 - \omega^2} d\omega'. \tag{5}$$

Here the sum over  $k$  includes only summation over all discrete excited states of the atom; the integration is carried out from the ionization threshold.

The natural generalization of the relation (1) for the  $2L$ -pole polarizability is given by Eq. (6):

$$\alpha_{2L}(\omega) = \sum_n \frac{2\omega_n |\langle 0 | M_{2L} | n \rangle|^2}{\omega_n^2 - \omega^2}, \tag{6}$$

where  $M_{2L}$  is the operator of the  $2L$ -pole moment of the system.



FIG. 1

<sup>1)</sup> A work appeared comparatively recently, [8] in which a method of calculation of the polarizability of the atoms is proposed, based on the use of the Green's function of the optical electron in the approximation of the quantum defect method.

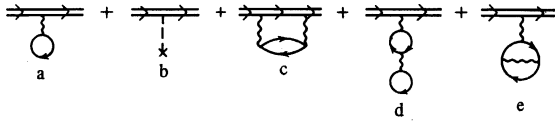


FIG. 2

3. The polarizability determines not only the cross section of the photoeffect. The interaction of a heavy, slow charged particle with a neutral atom at large distances is expressed in terms of the dipole static ( $\omega = 0$ ) polarizability: the polarization potential at large distances is  $-\alpha_d(0)/2r^4$ .<sup>[9]</sup> The interaction of the particle with an atom in the first two orders of perturbation theory is determined by the Coulomb interaction from graphs shown in Fig. 2. Here the heavy, slow, charged particle is shown by the double line and the Coulomb field of the nucleus by the dashed line with the cross. The wavy line denotes the Coulomb interaction with the electrons.

At large distances from the nucleus, all diagrams of the type of the Hartree self-consistent potential for the neutral atom (Figs. 2a, d, e) lead to a potential which decays exponentially with distance. The contribution of Fig. 2c determines the polarization potential at large distances and is equal to  $-\alpha_d(0)/2r^4$ . Account of the next orders in the interaction of the heavy, charged, slow particle with atomic electrons leads to terms in the potential  $U$  which fall off more rapidly with distance than  $1/r^4$ . These terms are no longer determined by the dipole, but by the quadrupole, etc., static polarizabilities. At small distances from the nucleus, the polarization potential described by the diagram of Fig. 2c is equal to

$$U(0) = - \sum_n \frac{| \langle 0 | r^{-1} | n \rangle |^2 }{ \omega_n } = - \frac{1}{2} \alpha_m(0). \quad (7)$$

We call this quantity the static "monopole" polarizability  $\alpha_m(0)$ . Knowledge of the "monopole" polarizability is necessary if we want to construct a potential that describes the interaction of a heavy, slow, charged particle with an atom at various distances.

By means of the static "monopole" polarizability, we can also express the correction to the energy of a deep hole level in terms of the interaction with the outer subshells. The correction to the energy of the hole is determined by the diagram shown in Fig. 3.

The corresponding correction to the energy level is

$$\Delta E = \sum_{\substack{i', k \leq F \\ i' > F}} \frac{ \langle i | V | i' k \rangle \langle i' k | V | i l \rangle }{ E_i - E_k - E_{i'} + E_l }. \quad (8)$$

If the radius of the  $i$ -th shell is much less than the radius of any of the  $k$ -th subshells, then it is possible to expand the Coulomb potential  $V$ , keeping only the principal term  $1/r$ . As a result, we get

$$\Delta E = \sum_{\substack{k \leq F \\ l > F}} \frac{ | \langle k | r^{-1} | l \rangle |^2 }{ E_l - E_k } = \frac{1}{2} \alpha_m(0), \quad (9)$$

i.e., the shift of the energy level is expressed in terms of the static "monopole" polarizability  $\alpha_m(0)$  of the external subshells of the atom. The natural generalization of the static "monopole" polarizability in the dynamic polarizability. It is determined by the relation

$$\alpha_m(\omega) = \sum_n \frac{ 2\omega_n | \langle 0 | r^{-1} | n \rangle |^2 }{ \omega_n^2 - \omega^2 }. \quad (10)$$

4. We consider the interaction of two neutral atoms at large distances. We shall assume that the ground states of the atoms are nondegenerate and both interacting atoms are in their ground states. In first order perturbation theory in the Coulomb interaction, there are four diagrams that describe the interaction of the nuclei and the electron shells with one another (Fig. 4).

As a consequence of the electron neutrality of each of the atoms, the total contribution of the diagrams shown in Fig. 4 is exponentially small at large distances.

In the next order in the interaction between the atoms A and B, there is a whole series of diagrams, shown in Fig. 5. The sum of all these diagrams except the last gives an exponentially small contribution between the atoms at large distances. So far as the last diagram is concerned, expanding the Coulomb potential  $V$  in powers of  $1/R$ , where  $R$  is the distance between the atoms A and B, and limiting ourselves to terms in  $1/R^3$ , we obtain the well-known result of London:

$$U(R) = - \frac{2}{3R^6} \sum_{n_A n_B} \frac{ l_{\max}^A l_{\max}^B | \langle 0 | r^A | n_A \rangle |^2 | \langle 0 | r^B | n_B \rangle |^2 }{ \omega_{n_A}^A + \omega_{n_B}^B } = \frac{C_6}{R^6}, \quad (11)$$

where  $l_{\max}$  is the largest of the quantum numbers  $l$  corresponding to the states  $\langle 0 |$  and  $| n \rangle$ . If we continue the expansion of the Coulomb potential  $V$  in powers of  $1/R$ , then the next will be not dipole-dipole, but quadrupole-dipole terms, which determine the contribution in  $U(R)$  proportional to  $1/R^8 - C_8/R^8$ .

5. In the Hartree-Fock approximation, the wave functions satisfy the equation:

$$\left( - \frac{\nabla^2}{2} - \frac{z}{r} + \sum_{j \leq F} \int \frac{ \varphi_j^*(r') \varphi_j(r') }{ |r - r'| } dx' \right) \varphi_k(r) - \sum_{j \leq F} \delta_{m_j, m_{jk}} \int \frac{ \varphi_j(r') \varphi_k(r') }{ |r - r'| } dx' \varphi_j(r) = E_k \varphi_k(r). \quad (12)$$

For  $k > F$ , the wave function describes the motion of the electron in the field of the neutral atom. Difficulties arise in the use of such wave functions, which are connected with the logarithmic divergence of the Coulomb

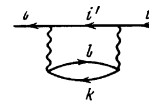


FIG. 3

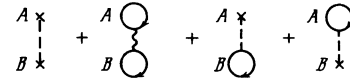


FIG. 4

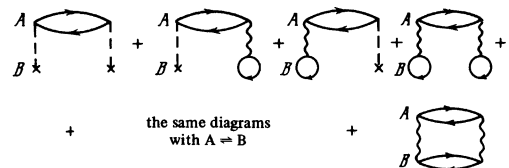


FIG. 5

matrix elements with  $l = 0$ , and which are diagonal with respect to the particle. These functions describe the forward scattering of the electron. In order to avoid these difficulties, we determine the wave function of the particle in the field of the atom without one electron.<sup>[10]</sup> For this purpose, it is necessary to discard the term  $j = i$  in Eq. (12) in the sum over  $j \leq F$ ; here  $i$  is the state in which the hole appeared. The effect of the excited electron on the frame is not taken into account, and in the calculation of the field which acts on it from the frame, the wave functions obtained for the ground state of the atom were used. Therefore, the single Hartree-Fock equation without self-consistency, is found for the wave function of the excited electron. The functions of the excited states are orthogonalized to functions of the occupied states having the same value of the orbital momentum  $l$ . As was shown in<sup>[10]</sup>, such a determination of the wave function is equivalent to account of the share of many-electron correlations. The calculations were carried out according to the programs published in<sup>[11]</sup>.

6. As was shown in<sup>[10]</sup>, in medium and heavy atoms, one can use the high-density approximation. For account of the many-electron correlations, we used the random phase method with exchange.

The polarizability with account of many-electron effects in the random phase approximation with exchange is determined by an infinite series of diagrams shown in Fig. 6. The case is similar for the Van der Waals energy of interaction between atoms A and B (Fig. 7). The cross-hatched square in Figs. 6 and 7 indicates the amplitude of the interaction which, in the random phase approximation with exchange satisfies the following equation:

$$\langle k_1 k_3 | \Gamma(\omega) | k_2 k_4 \rangle = \langle k_1 k_3 | U | k_2 k_4 \rangle - \left( \sum_{\substack{k_1 < F \\ k_1 > F}} - \sum_{\substack{k_2 > F \\ k_2 < F}} \right) \frac{\langle k_1 k_3 | U | k_2 k_4 \rangle \langle k_2 k_3 | \Gamma(\omega) | k_4 k_1 \rangle}{\omega - E_{k_3} + E_{k_4} + i\delta(1 - 2n_{k_3})}, \quad (13)$$

where the index  $k_i$  denotes the set of four quantum numbers  $n, l, m, s$ ,

$$\langle k_1 k_3 | U | k_2 k_4 \rangle = \langle k_1 k_3 | V | k_2 k_4 \rangle - \langle k_1 k_3 | V | k_2 k_4 \rangle, \quad (14)$$

$\langle k_1 k_3 | V | k_2 k_4 \rangle$  is the Coulomb matrix element,

$$\langle k_1 k_3 | V | k_2 k_4 \rangle = \int \varphi_{k_1}^*(\mathbf{r}_1) \varphi_{k_3}^*(\mathbf{r}_2) \varphi_{k_2}(\mathbf{r}_1) \varphi_{k_4}(\mathbf{r}_2) \frac{d\mathbf{r}_1 d\mathbf{r}_2}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (15)$$

$n_{k_5}$  is the Fermi step,

$$n_{k_5} = \begin{cases} 1, & k_5 \leq F \\ 0, & k_5 > F \end{cases}$$

The condition  $k_5 \leq F$  denotes summation over the occupied states,  $k_5 > F$  the summation over the free states,

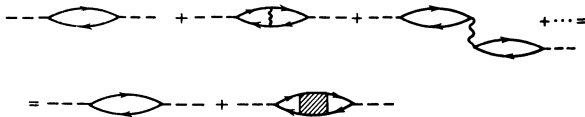


FIG. 6

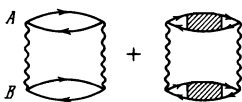


FIG. 7

including integration over the continuous spectrum.

Separating the angular variables in Eq. (13), we transform to the reduced matrix elements, obtaining as a result

$$\langle n_1 l_1 n_2 l_2 | \Gamma_i(\omega) | n_2 l_2 n_1 l_1 \rangle = \langle n_1 l_1 n_2 l_2 | U_i | n_2 l_2 n_1 l_1 \rangle - \left( \sum_{\substack{n_1 < F \\ n_1 > F}} - \sum_{\substack{n_2 > F \\ n_2 < F}} \right) \langle n_1 l_1 n_2 l_2 | U_i | n_2 l_2 n_1 l_1 \rangle \langle n_2 l_2 n_1 l_1 | \Gamma_i(\omega) | n_2 l_2 n_1 l_1 \rangle \cdot \cdot \{(2l+1)[\omega - E_{n_1} + E_{n_2} + i\delta(1 - 2n_{k_5})]\}^{-1}. \quad (16)$$

The method of solution of Eq. (16) is described in<sup>[10,11]</sup>. The error in the solution of the equation is  $\sim 5\%$ .

In correspondence with Fig. 6, the reduced dipole matrix element in the account of the many-electron correlations is written in the following fashion:

$$\langle n_1 l_1 | d(\omega) | n_2 l_2 \rangle + \sum_{\substack{n_1 < F \\ n_1 > F}} \frac{1}{3} \left( \frac{\langle n_1 l_1 | d | n_2 l_2 \rangle \langle n_1 l_1 n_2 l_2 | \Gamma_i(\omega) | n_2 l_2 n_1 l_1 \rangle}{\omega - E_{n_1} + E_{n_2} + i\delta} - \frac{\langle n_2 l_2 | d | n_1 l_1 \rangle \langle n_2 l_2 n_1 l_1 | \Gamma_i(\omega) | n_1 l_1 n_2 l_2 \rangle}{\omega - E_{n_2} + E_{n_1} - i\delta} \right), \quad (17)$$

where  $\omega = E_{n_1} - E_{n_2}$  ( $n_1 < F, n_2 \leq F$ ) and the reduced dipole matrix element is defined in the following way:

$$\langle n_1 l_1 | d | n_2 l_2 \rangle = \sum_{m=-1}^1 \begin{pmatrix} l_1 & 1 & l_2 \\ -m_1 & m & m_2 \end{pmatrix} (-)^{m_1} \langle n_1 l_1 | d | n_2 l_2 \rangle. \quad (18)$$

The dipole polarizability and the London energy of interaction of atoms with account of many-electron correlations is determined by the formulas (1) and (11), in which we must substitute the sum (17) in place of the dipole matrix elements.

Formulas are obtained in similar fashion for the "monopole" and quadrupole polarizabilities with account of many-electron corrections.

7. One can determine the dipole polarizability in two representations—in terms of the coordinate operator  $\mathbf{r}$  or the operator  $\nabla$ . In the Hartree-Fock approximation, because of the presence of the nonlocal operator, the sum rule is not satisfied for the oscillator strengths and  $\sigma_d^r$  is not identical with  $\alpha_d^\nabla$ . In the exact statement of the problem, as well as in the random phase approximation with exchange, both definitions should give the same result.<sup>[10]</sup> The calculation was carried out by means of Eq. (5), where  $(F_k, \sigma)_r$ ,  $(F_k, \sigma)_\nabla$ ,  $(F_k, \sigma)_r$  RPAE and  $(F_k, \sigma)_\nabla$  RPAE (RPAE = random phase approximation with exchange) have been successfully substituted.

The decisive contribution to the dipole dynamic polarizability of the noble gas atoms Ne, Ar, Kr and Xe is made by transitions of electrons with the upper filled p-subshell in the continuous spectrum in the d state. The contribution from transitions of electrons to the discrete spectrum amounts to 10–20%. Transitions with the highest occupied p subshell at the discrete s level are the principal ones. Before account is taken of the correlations, the difference of  $\alpha_d^r$  and  $\alpha_d^\nabla$  is quite great. After taking account of the many-electron correlations, the difference between the  $r$  and  $\nabla$  representations has practically vanished (in the limits of the technical errors of the calculation). The resultant data for the static dipole polarizability are shown in Table I, where they are compared with the experimental values of  $\alpha_d(0)$ .<sup>[12]</sup>

TABLE I

	$\alpha_d^r(\omega)$	$\alpha_d^y(\omega)$	$\alpha_d^{\text{RPAE}}(\omega)$	$\alpha_d^{\text{semiemp(0)}}$ from [13]
Ne	2.47	1.88	2.30	2.663
Ar	12.39	7.40	10.73	11.080
Kr	18.98	11.15	16.18	16.734
Xe	32.45	17.25	27.98	27.292

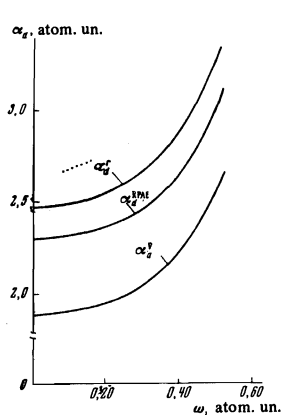


FIG. 8

FIG. 8. Dipole dynamic polarizability of the Ne atom. The points are the experimental values of [13].

FIG. 9. Dipole dynamic polarizability of the Ar atom. 1— $\alpha_d^r$ , 2— $\alpha_d^y$ , 3— $\alpha_d^{\text{RPAE}}$ . The points are the experimental values of [13].

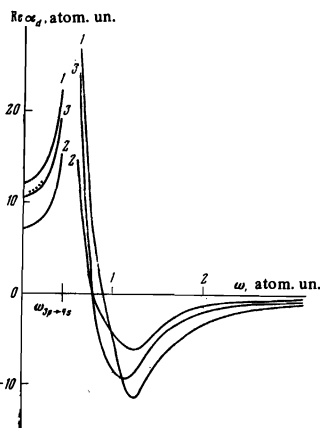


FIG. 9

Figures 8–10 give the results of calculations of the dipole dynamic polarizability for Ne, Ar, Kr and Xe, which are compared with the experimental data on the indices of refraction. [13] The index of refraction  $n(\omega)$  is connected with the polarizability by the well-known formula  $(n^2(\omega) - 1)/(n^2(\omega) + 2) = (4/3)\pi N\alpha(\omega)$ , where  $N$  is the number of atoms in  $1 \text{ cm}^3$ . For standard temperature and pressure,  $N = 0.2687 \times 10^{20} \text{ atoms/cm}^3$ . The experimental values are shown as points.

It is seen that the calculation of  $\alpha_d$  in the RPAE approximation is found to be in excellent agreement with experiment for all atoms with the exception of Ne. The difference between the values of the dipole polarizability of Ne, calculated by the Hartree-Fock method, and its experimental values has been noted previously. [4,14,15]

The method used in the present research makes it possible to calculate the polarizability even in the vicinity of discrete levels of excitation, i.e., the poles of the expression (1). In this region,

$$\alpha(\omega) = \frac{F_n}{\omega_n^2 - \omega^2} + \alpha_d'(\omega_n).$$

Existing programs allow us to compute both  $F_n$  and  $\omega_n$  for a number of first levels, and also the values of  $\alpha_d'(\omega_n)$ . For example, in the vicinity of the 4s level in Ar, the value of  $F_n = 0.294$ ,  $\alpha_d'(\omega_n) = 14.81$ ,  $\omega_n = 0.45$ . The existing programs also allow us to compute the polarizability or, more exactly, its real part at energies  $\omega$  exceeding the ionization potential in the region where, by definition  $\omega \text{ Im } \alpha(\omega) = 4\pi c^{-1} \sigma(\omega)$ . The results of the calculation of  $\text{Re } \alpha_d$  for Ar is shown in Fig. 9.

Figure 11 shows the results of the calculation of the quadrupole and “monopole” dynamic correlations for

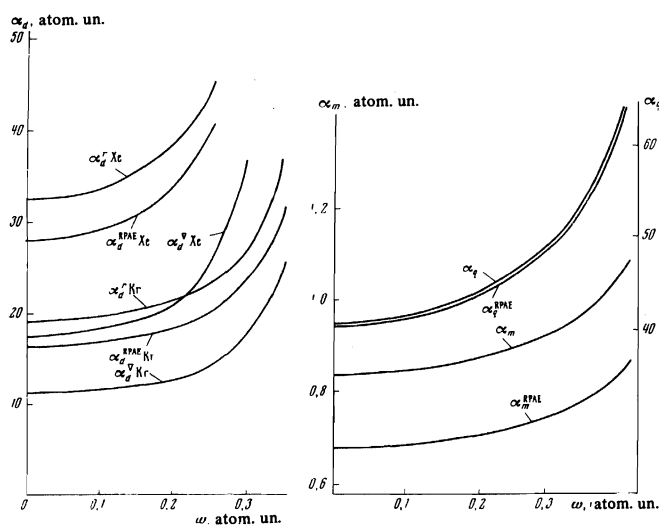


FIG. 10

FIG. 11

FIG. 10. Dipole dynamic polarizability of atoms Kr and Xe.

FIG. 11. “Monopole” and quadrupole dynamic polarizability of the Ar atom.

Ar. It is seen that the effect of many-electron correlations on the quadrupole polarizability is small while their effect on the “monopole” polarizability is very large.

The greatest contribution to the quadrupole polarizability is made by transitions with the upper occupied p subshell in the continuous spectrum in the f state. However, in contrast with the dipole polarizability, the contribution from transitions of electrons in the discrete spectrum rose sharply ( $\sim 30\text{--}40\%$  of the total value). As was pointed out above, the shift in the deep hole level due to interaction with external electrons is expressed in terms of the “monopole” polarizability. The Hartree-Fock calculation gives for the energy of the 1s, 2s and 2p levels in Ar, the respective values 237.22 Ry, 24.64 Ry and 19.14 Ry. After account of interaction with external electrons, one obtains 235.82 Ry, 23.96 Ry and 18.46 Ry. Experiment [16] gives 235.76 Ry for the 1s and 24.01 Ry for the 2s level. The 2p level splits into 18.43 Ry and 18.27 Ry. It is seen that such an account of the interaction of the deep electron with the external ones sharply decreases the difference between the calculated and experimental value of the energy of the level.

Knowing the value of the static “monopole” polarizability, we can determine the polarization potential at zero by Eq. (7) and can therefore calculate the value of the constant  $S$  in the Bates formula for polarization potential  $U(r) = \alpha_d/2(r^2 + S^2)^2$ . The value of  $S$  for Ar is equal to  $1.98a_0$ , which is significantly larger than the value of  $S$  which follows from estimates from the Thomas-Fermi model. For oxygen, according to [7] the value of  $S$  is also much greater than follows from estimates based on the statistical model. [17]

We have carried out the calculation of the coefficients  $C_6$  and  $C_8$  of the interaction potential between two noble gas atoms both in the single-electron approximation and with account of many-electron correlations. The results for  $C_6$  are shown in Table 2. It is seen that the effect of

Table II

Pairs	$C_6^r$	$C_6^\nabla$	$C_6^{\text{RPAE}}$	$C_6^{\text{semiemp}}$ [14]	Pairs	$C_6^r$	$C_6^\nabla$	$C_6^{\text{RPAE}}$	$C_6^{\text{semiemp}}$ [14]
Ne — Ne	10.42	5.17	7.9	7.99	Ar — Kr	169.48	44.38	100.3	91.8
Ne — Ar	34.28	12.50	23.4	21.9	Ar — Xe	241.96	58.24	137.4	129.9
Ne — Kr	45.12	16.52	30.0	28.6	Kr — Kr	231.45	59.23	132.3	125.8
Ne — Xe	62.75	21.4	39.8	39.0	Kr — Xe	330.85	78.00	181.1	180.1
Ar — Ar	124.66	33.46	77.1	67.8	Xe — Xe	479.66	103.59	250.6	261.9

the correlations, which reveal themselves in the difference of  $C_6^r$  and  $C_6^\nabla$ , is large. Account of correlations leads to coincidence of  $C_6^{\text{RPAE}}$  and  $C_6^{\nabla\text{RPAE}}$ . Calculation of  $C_8$  for the interaction of two Ar atoms gave  $C_8^{\text{HF}} = 744$  and  $C_8^{\text{RPAE}} = 596$ . The relation between  $C_6$  and  $C_8$  shows that the expansion of the interaction potential of the atoms Ar-Ar in powers of  $1/R$  is valid at distances much greater than  $3a_0$ .

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Translated by R. T. Beyer

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