Dispersion forces by means of the variational method

A. Kh. Kyarov and A. I. Temrokov

Department of Theoretical Physics, Kabardino–Balkarian State University, 360004 Nalchik, Russia

(Submitted 24 December 1993; resubmitted 14 March 1994)
Zh. Eksp. Teor. Fiz. **106**, 69–76 (July 1994)

We suggest a model for calculating the van der Waals constant C_6 for a pair of atoms of inert gases by means of the density-functional method. The calculated dispersion constants agree well with the experimental data.

INTRODUCTION

A model for calculating dispersion forces using the density-functional method (DFM) was suggested in Ref. 1. The correction $\delta\rho(\mathbf{r})$ to the electron density in an atom in the presence of an external perturbing potential $S(\mathbf{r})$ is given by the following formula:

$$\delta\rho(\mathbf{r})=\frac{\lambda}{\pi}\left(\frac{3}{\pi}\right)^{1/3}\rho^{1/3}(\mathbf{r})S(\mathbf{r}), \tag{1}$$

where $\rho(\mathbf{r})$ is the electron density in the unperturbed atom.

The calculations carried out in Ref. 1 of the coefficients of dispersion dipole–dipole forces of ions in alkali-halide crystals yielded results that lay between the values obtained in Refs. 2 and 3, with the exception of sodium-halide crystals.

Calculations for different pairs of atoms of inert gases using the expressions obtained in Ref. 1 yield values of the dispersion constant C_6 10 to 100 times greater than values obtained through experiments (for the case where the electron distribution in an atom in the ground state is assumed to be of the Hartree–Fock type).

We believe that attempts to decrease C_6 by introducing a limit on the electron density radius (equivalent to the absence of a strong overlap of the electron clouds of the interacting atoms[1]) is not entirely justified and leads to an asymptotic dependence of the dispersion constant on the separation between the atomic nuclei.

1. A MODEL FOR CALCULATING C_6 IN THE DFM

Consider two neutral atoms separated by a distance R much larger than the atomic dimensions $l_{1,2}$. For $R \gg l_{1,2}$, we must allow only for the dipole–dipole interaction between the atoms in the first approximation , with the corresponding interaction energy[4]

$$U=\frac{\langle\hat{\mathbf{d}}_1\rangle\langle\hat{\mathbf{d}}_2\rangle-3(\langle\hat{\mathbf{d}}_1\rangle\mathbf{n})(\langle\hat{\mathbf{d}}_2\rangle\mathbf{n})}{R^3}, \tag{2}$$

where $\langle\hat{\mathbf{d}}_1(\mathbf{r}_1,t)\rangle$ and $\langle\hat{\mathbf{d}}_2(\mathbf{r}_2,t)\rangle$ are the average dipole moments of atoms 1 and 2, which at time t are at points $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively, $\mathbf{R}=\mathbf{r}_2-\mathbf{r}_1$, and $\mathbf{n}=\mathbf{R}/R$. By average we mean quantum mechanical and statistical averages.

For two neutral atoms in the ground state the average dipole moments are zero and the interaction energy (2) vanishes. In such conditions the dipole moments $\mathbf{d}_1$ and $\mathbf{d}_2$, whose averages are zero, contribute to the interaction only owing to fluctuations.

Let us assume that in atom 1 a fluctuation moment $\mathbf{d}_1{}^{\mathrm{sp}}(\mathbf{r}_1,t)$ spontaneously emerges which generates a field $\mathbf{E}_1(\mathbf{r},t)$. In the other atom, 2, this field induces a dipole moment

$$\mathbf{d}_2{}^{\mathrm{ind}}(\mathbf{r}_2,t)=\alpha_2\mathbf{E}_1(\mathbf{r}_2,t), \tag{3}$$

where α_2 is the dipole–dipole polarizability of atom 2.

The field $\mathbf{E}_1(\mathbf{r}_2,t)$ is the electric field generated by the dipole moment of the first atom, $\mathbf{d}_1{}^{\mathrm{sp}}(\mathbf{r}_1,t)$, at the point where atom 2 is situated:

$$\mathbf{E}_1(\mathbf{r}_2,t)=\frac{3\mathbf{n}(\mathbf{d}_1{}^{\mathrm{sp}}(\mathbf{r}_1,t)\mathbf{n})-\mathbf{d}_1{}^{\mathrm{sp}}(\mathbf{r}_1,t)}{R^3}. \tag{4}$$

Similarly, a dipole moment $\mathbf{d}_2{}^{\mathrm{sp}}(\mathbf{r}_2,t)$ that spontaneously emerges in the second atom generates a dipole moment $\mathbf{d}_1{}^{\mathrm{ind}}(\mathbf{r}_1,t)=\alpha_1\mathbf{E}_2(\mathbf{r}_1,t)$ in the first.

The interaction energy can be written as

$$U(R)=-\tfrac{1}{2}\langle\mathbf{d}_2(\mathbf{r}_2,t)\mathbf{E}(\mathbf{r}_2,t)\rangle, \tag{5}$$

where $\mathbf{d}_2(\mathbf{r}_2,t)$ is the total fluctuation dipole moment of the second atom, taking into account both the spontaneous fluctuation term and the fluctuation term induced by the first atom, and $\mathbf{E}(\mathbf{r}_2,t)$ is the total fluctuation electric field at the point occupied by the second atom.

For systems with fairly high symmetry, for instance, for spherically symmetric atoms of inert gases, the dipole–dipole interaction energy has the form

$$U(R)=-C_6R^{-6}. \tag{6}$$

The main assumptions underlying this model are:

a) The $\langle\mathbf{d}_i{}^{\mathrm{sp}}(t),\mathbf{d}_j{}^{\mathrm{sp}}(t')\rangle$ correlation functions that describe the temporal correlations of the spontaneous fluctuations of the components of the dipole moment in each atom are zero.

b) A fluctuation dipole moment is generated by a fluctuation in the electron density of the atom, whose time-average has the form

$$\delta\rho(\mathbf{r})=k\rho(\mathbf{r})\cos\theta, \tag{7}$$

where k is a parameter ($k \ll 1$), θ is the angle between vectors $\mathbf{r}_i$ and $\mathbf{R}$, with $\mathbf{r}_i$ the radius vector connecting the center of the nucleus and the ith electron, and $\rho(\mathbf{r})$ is the electron density of the atom.

1063-7761/94/070035-04$10.00

Choosing the fluctuations of the electron density in the form (7) yields a finite dipole moment and conserves the normalization condition imposed on the electron density of the atom.

The standard procedure for minimizing the energy functional in the perturbation leads to the following value for the perturbation energy:

$$\delta E=\delta V_{\rm en}+\delta V_{\rm ee}+\delta T+\delta W_k+\delta V_{\rm ex}, \tag{8}$$

$$\delta V_{\rm en}=-\frac{kZ}{2}\int\frac{D(r)}{r}\,dr \tag{9}$$

is the electron–nucleus part, with Z the nuclear charge, and $D(r)=4\pi r^2\rho(r)$;

$$\delta W_k=\frac{2}{3}\frac{k^2}{72}\int\frac{D(r)}{r^2}\,dr \tag{10}$$

is the quantum correction;

$$\delta T=\delta T_1+\delta T_2$$

$$=-\frac{5\kappa_k}{(4\pi)^{2/3}}\,k\left(\frac{1}{6}+\frac{k}{27}\right)\int\frac{[D_{(r)}^{5/3}]}{r^{4/3}}\,dr \tag{11}$$

is the kinetic energy;

$$\delta V_{\rm ex}=\delta V_{\rm ex1}+\delta V_{\rm ex2}$$

$$=-\frac{2\kappa_e}{3(4\pi)^{1/3}}\,k\left(1+\frac{k}{9}\right)\int\frac{[D_{(r)}^{4/3}]}{r^{2/3}}\,dr \tag{12}$$

is the exchange energy; and

$$\delta V_{\rm ee}=\alpha kC_1+k^2C_1 \tag{13}$$

is the electron–electron part, with

$$C_1=\frac{1}{12}\int_0^\infty\frac{D(r)}{r^2}\,dr$$

$$\times\left\{\int_0^r[(r^2+r')^{3/2}-r^3]\,\frac{D(r')}{r'^2}\,dr'\right.$$

$$\left.+\int_0^\infty[(r^2+r'^2)^{3/2}-r'^2]\,\frac{D(r')}{r'^2}\,dr'\right\}. \tag{14}$$

The minimum condition $\delta E/\delta k=0$ yields the value

$$k=\frac{\delta V'_{\rm en}-2C_1-2/9\delta T'_1+9\delta V'_{\rm ex1}}{2(\delta W'_k+\delta T'_2+C_1-\delta V'_{\rm ex2})}, \tag{15}$$

where the subscripts 1 and 2 stand for the first and second terms in Eqs. (11) and (12), respectively, and the primes indicate the absence in the expressions of the factor k or k^2. Here the minimum energy value is

$$\delta E_{\rm min}=-\frac{(\delta V'_{\rm en}-2C_1-2/9\delta T'_1+9\delta V'_{\rm ex1})^2}{4(\delta W'_k+\delta T'_2+C_1-\delta V'_{\rm ex2})}. \tag{16}$$

Equation (15) determines the variational parameter k and, hence, the fluctuation dipole moment:

$$\mathbf{d}_1(\mathbf{r}_1)=\int\mathbf{r}\delta\rho_1(\mathbf{r})\,dr. \tag{17}$$

Allowing for the fact that $\mathbf{r}=|\mathbf{r}|\mathbf{n}\cos\theta$, we get

$$\mathbf{d}_1(\mathbf{r}_1)=\mathbf{n}\int|\mathbf{r}|k\rho_1(\mathbf{r})\cos^2\theta\,d^3r. \tag{18}$$

If we now combine Eqs (3)–(5) and (18) and integrate with respect to the angular variables, we obtain

$$U(\mathbf{R})=-\frac{2}{R^6}\left\{\alpha_2k_1^2\left[\frac{1}{3}\int rD_1(r)\,dr\right]^2\right.$$

$$\left.+\alpha_1k_2^2\left[\frac{1}{3}\int rD_2(r)\,dr\right]^2\right\}, \tag{19}$$

where k_1 and k_2 are the values of the variational parameters for atoms 1 and 2, and α_1 and α_2 the polarizabilities of atoms 1 and 2.

Employing Eq. (6), we arrive at an expression for the van der Waals constant for heteroatomic pairs,

$$C_6=2\left\{\alpha_2k_1^2\left[\frac{1}{3}\int rD_1(r)\,dr\right]^2\right\{+\alpha_1k_2^2\left[\frac{1}{3}\int rD_2(r)\,dr\right]^2\right\}, \tag{20}$$

or, allowing for the fact that

$$\int rD(r)\,dr=\langle r\rangle, \tag{21}$$

where $\langle r\rangle$ is the average radius, we get

$$C_6=\tfrac{2}{9}\{\alpha_2k_1^2\langle r_1\rangle^2+\alpha_1k_2^2\langle r_2\rangle^2\}. \tag{22}$$

For homoatomic pairs we have

$$C_6=\tfrac{4}{9}\alpha_1k_1^2\langle r_1\rangle^2. \tag{23}$$

Thus, to determine the dispersion constants self-consistently we must know how to determine polarizabilities in the DFM.

2. CALCULATING THE ATOMIC POLARIZABILITIES IN THE DFM FOR INFINITELY DISTRIBUTED ELECTRON DENSITIES

Statistical theory has been used to derive an expression for calculating the polarizability α in the form:[5]

$$\alpha=\frac{K^2(r_0)}{2\int_0^{r_0}K(r)[\rho(r)]^{1/3}r\,dr+(5\kappa_k/6\pi e^2)\,K(r_0)}, \tag{24}$$

where

$$K(r)=\int_0^r[\rho(r')]^{1/3}r'^4\,dr', \tag{25}$$

and r_0 is the "boundary" value of the atomic radius.

Equation (24) was derived without taking into account the exchange, quantum, and correlation corrections since these are small compared to the kinetic and Coulomb parts of the perturbing potential, the latter having the same sign in the case at hand.

The polarizabilities of inert gas atoms calculated according to Eq. (24) with an electron distribution minimizing the energy functional exceed the experimental values by a factor of 10 to 100, which suggests that Eq. (24) is inapplicable for "infinitely distributed" electron densities of the Hartree–Fock type. This necessitates obtaining a new, more universal, formula for calculating the polarizability of atoms.

To this end let us consider the physical principles developed in Ref. 5 that led to Eq. (25). Most interesting here is that the perturbed electron density was chosen in the form[5]

$$\rho' = \rho\left(1 + \lambda \frac{v_s - v_0}{V^* - V_0}\right), \tag{26}$$

$$v_0 = \left(\int v_s \rho^{1/3}\, d\mathbf{r}\right)\left(\int \rho^{1/3}\, d\mathbf{r}\right)^{-1}, \tag{27}$$

where λ is a variational parameter, V^* the electron–nucleus potential, and V_0 a Lagrange multiplier. Then the perturbation is

$$\delta\rho = \lambda \frac{v_s - v_0}{V^* - V_0}\rho = \frac{3e}{5\kappa_k}\lambda(v_s - v_0)\rho^{1/3}, \tag{28}$$

which leads us to Eq. (24) for the polarizability.

That we have chosen $\delta\rho$ in the form (28) follows, generally speaking, from the Thomas–Fermi equation with the Amaldi correction,[5] but clearly the choice of $\delta\rho$ in the variational method is very arbitrary, the more so if the DFM approach is broader than the Thomas–Fermi model.

On the other hand, the expression for the perturbed density in the simple form

$$\rho' = \rho[1 + \lambda(v_s - v_0)] \tag{29}$$

is inapplicable in the Thomas–Fermi model (see Ref. 5) because the values of the derived polarizabilities are too small, since Eq. (29) ignores the fact that the perturbation most strongly deforms the outer, weakly bound, regions of the atom. This is reflected in the fact that (28) contains $V^* - V_0$ in the denominator, and this difference rapidly decreases as we move away from the nucleus.

The above ideas are valid, however, only for electron densities within a region of a certain radius r_0. In the case of "quasi-Hartree–Fock" densities the denominator $V^* - V_0$ tends to zero so rapidly at great distances that the asymptotically small values of the electron density far from the nucleus provide a large contribution and lead to polarizability values overestimated by a factor of 10 to 100. This suggests that the perturbation of the weakly bound outer region of an atom cannot be described by Eq. (26) and it is natural to use the expression (29) for the perturbed electron density.

Of course, specifying the "inner" and "outer" atomic regions in the statistical model is extremely arbitrary. Hence, a self-consistent approach must contain the possibility of such division. In this paper the perturbation of the electron density of an atom is chosen in the form

$$\delta\rho = \delta\rho_1 + \delta\rho_2, \tag{30}$$

where

$$\delta\rho_1 = \frac{3e}{5\kappa_k}\lambda_1 v_s \rho^{1/3}(r)\theta(r_0 - r), \tag{31}$$

$$\delta\rho_2 = \kappa_k \kappa_e^{3/2} \lambda_2 v_s \rho(r)\theta(r - r_0); \tag{32}$$

here λ_1 and λ_2 are variational parameters, $\theta(x)$ the is Heaviside step function, and v_s is the external electric field (perturbation).

The factor $\kappa_k \kappa_e^{3/2}$ in (32) was selected for dimensional considerations. In this approach, r_0 is the radius that divides the atom into "inner" ($r < r_0$) and "outer" ($r > r_0$) regions.

From the continuity condition imposed on $\delta\rho(r)$ at $r = r_0$ we obtain

$$\rho(r_0) = \left(\frac{\lambda_1(r_0)}{\lambda_2(r_0)}\frac{3}{5\kappa_k^2 \kappa_e^{3/2}}\right)^{3/2}, \tag{33}$$

or for $D(r) = 4\pi r^2 \rho(r)$,

$$D(r_0) = 4\pi r_0^2 \left(\frac{\lambda_1(r_0)}{\lambda_2(r_0)}\frac{3}{5\kappa_k^2 \kappa_e^{3/2}}\right)^{3/2}. \tag{34}$$

The continuity condition imposed on the derivative of $\delta\rho$ at $r = r_0$ makes $D(r_0)$ proportional to r_0^2, which is similar to (34).

The standard variational procedure[5] makes it possible to determine the parameters λ_1 and λ_2:

$$\begin{aligned}\lambda_1(r_0) = K(r_0)\Bigg[\frac{8\pi e^2}{5\kappa_k}\Bigg\{\int_0^{r_0} K(r)[\rho(r)]^{1/3} r\, dr \\ + \int_0^{r_0} dr\, r^4 [\rho(r)]^{1/3} \int_r^{r_0} dr' r' [\rho(r')]^{1/3}\Bigg\} \\ + \frac{2}{3}K(r_0)\Bigg]^{-1}\end{aligned} \tag{35}$$

$$\begin{aligned}\lambda_2(r_0) = \frac{3}{\kappa_k \kappa_e^{3/2}}\left(\int_{r_0}^{\infty} r^2 D(r)\, dr\right)^2 \Bigg[1.5\int_{r_0}^{\infty} dr \frac{D(r)}{r} \\ \times \Bigg\{\int_{r_0}^{r} \frac{D(r')}{r'}[(r^2 + r'^2)^{3/2} - r^3]\, dr' \\ + \int_r^{\infty} \frac{D(r')}{r'}[(r^2 + r'^2)^{3/2} - r'^3]\, dr'\Bigg\} \\ + (0.75\pi)^{2/3}\int_{r_0}^{\infty} \frac{D^{5/3}(r)}{r^{4/3}}\, dr\Bigg]^{-1}.\end{aligned} \tag{36}$$

Using (35) and (36) with (34), we can find r_0, with the polarizability

$$\alpha_1 = \alpha_{11} + \alpha_{12}, \tag{37}$$

where

$$\alpha_{11} = \frac{4\pi}{5\kappa_k}\lambda_1(r_0)K(r_0), \tag{38}$$

$$\alpha_{12} = \frac{\kappa_k \kappa_e^{3/2}}{3}\lambda_2(r_0)\int_{r_0}^{\infty} r^2 D(r)\, dr. \tag{39}$$

TABLE I. Polarizabilities (in units of $10^{-24}\,\mathrm{cm}^{-3}$).

Atom Method	He	Ne	Ar	Kr
Thomas–Fermi model[5] (Eq. (24))		2.01	2.88	400.
Suggested model	0.226	0.413	1.51	2.22
Experiment (Ref. 6)		0.392	1.65	2.50
Experiment (Ref. 7)	0.201	0.390	1.62	2.46

In this model we did not allow for the electron–electron Coulomb interaction between the "inner" and "outer" electrons. Estimates have shown that allowing for this interaction has little effect on the results for atoms with a small number of electrons.

Table I lists the results in different models and the experimental data on the polarizability of atoms of inert gases. The discrepancy between the values calculated in the present model and the experimental polarizability values is roughly 10%, which suggests that the assumptions underlying our model are true. The accuracy of calculations for all the atoms is roughly the same, although the errors have different signs. The statistical nature of the model, which raises the probability of agreement with the experimental data as the number of electrons increases, has no effect on the result. The reason is the growth in the contribution of the electron–electron interaction between the "inner" and "outer" electrons, a factor not taken into account by the model.

The results of calculations of C_6 for different pairs of atoms of inert gases that incorporated the polarizabilities obtained in this paper and the quasi-Hartree–Fock electron densities[8] are listed in Table II.

Comparison of the dispersion constants calculated by means of this model and the experimental data of Ref. 9 proves that the present approach to calculating C_6 is justified. On the whole, the deviation from the exact values is less than 10% (30% for the He–He pair). The maximum deviations in homoatomic van der Waals constants for the He–He and Kr–Kr pairs are explained, for the first pair, by the statistical nature of the computation model and, for the second, by the increase in the contributions (not allowed for by the model) from the higher-order terms in the perturbation-theory expansion for the energy, and also by the fact that we ignored the differences in the binding energies of the valence and atomic-core electrons in Eq. (7) and did not allow for the correlation energy. We believe that allowing for the these contributions can improve the agreement between the calculated C_6 and the experimental data.

We conclude with a few details about the reasons for choosing the time-average of the electron-density fluctuation in the form (7). In addition to those listed in Sec. 1, an obvious reason is the great simplicity and convenience of (7) for calculations. Clearly, allowing for the differences in the binding energies of the valence and atomic-core electrons requires choosing $\delta\rho$ in (7) the way it was done in (30). But we can also say that $\delta\rho$ in (7) is chosen in the first approximation in the form (30) with $r_0=0$.

TABLE II. Values of the dispersion constant C_6 (in atomic units).

Pairs of atoms	Calculated values	Upper and lower bounds
He–He	0.9754	1.44–1.47
Ne–Ne	6.59	6.48–7.27
Ar–Ar	72.68	63.6–70.8
Kr–Kr	176.84	124–142
He–Ne	2.7	3.03–3.20
He–Ar	8.70	9.43–10.1
He–Kr	13.81	13.0–14.2
Ne–Ar	21.98	19.5–22.0
Ne–Kr	34.16	26.5–30.9
Ar–Kr	113.58	88.6–100

At present we are doing calculations that use the time-average of the fluctuations of the electron density of an atom in the form $\delta\rho=\delta\rho_1+\delta\rho_2$, with $\delta\rho_1 \sim \rho^{1/3}\theta(r_0-r)$ and $\delta\rho_2 \sim \rho\theta(r-r_0)$, and that generalize the model suggested in this paper. Final results, however, are yet to be obtained.

This model for calculating C_6 is entirely different from that developed in Ref. 1, where the external perturbing potential enters into the expression for the correction to the electron density of the unperturbed atom (Eq. (1)).

The model of Ref. 1 is unsuitable for atoms with an electron distribution of the Hartree–Fock type, and basically for any known distribution of electron densities (Thomas–Fermi, Thomas–Fermi–Dirac, etc.) yields only the upper bounds on the dispersion constants. The smaller the boundary value of the radius of the electron cloud in the theory, the more reasonable is the result obtained in the model of Ref. 1. The model suggested in this paper can be used for any atoms with a spherically symmetric distribution of the electron density because no other suggestions linking our model precisely with atoms of inert gases have been made.

[1] G. V. Dedkov and A. I. Temrokov, Fiz. Tverd. Tela (Leningrad) **21**, 1218 (1979) [Sov. Phys. Solid State **21**, 706 (1979)].

[2] J. E. Mayer, J. Chem. Phys. **1**, 270 (1933).

[3] P. A. Harris, Chem. Phys. Lett. **33**, 495 (1975).

[4] Yu. S. Barash, *Van der Waals Forces*, Nauka, Moscow, 1988 (in Russian).

[5] P. Gombás, *Die Statistische Theorie des Atoms und ihre Anwendungen*, Springer, Vien, 1949.

[6] K. Fajans and G. Joos, Z. Phys. **23**, 1 (1924).

[7] L. Pauling, Proc. R. Soc. London **114**, 181 (1927).

[8] T. G. Strand and R. A. Bonham, J. Chem. Phys. **40**, 1686 (1964).

[9] J. M. Strandard and P. R. Certain, J. Chem. Phys. **83**, 3002 (1985).

Translated by Eugene Yankovsky

This article was translated in Russia. It is reproduced here with all the stylistic changes by the Translation Editor and the Editor of the Russian text.