APPLICATION OF THE FOCK EXPANSION IN THE THEORY OF VAN DER WAALS FORCES

PHYSICS

1968

SovietRxiv

Abstract

Full Text

UDC 539.186.3

PHYSICS

A. V. TULUB

APPLICATION OF THE FOCK EXPANSION IN THE THEORY OF VAN DER WAALS FORCES

(Presented by Academician V. A. Fock on 1 II 1968)

For calculating the van der Waals interaction energy between neutral atoms due to the so-called dispersion forces, one may use the direct variational method for the second correction to the energy of the unperturbed system, i.e., the system of two free atoms. Such a calculation requires knowledge of the atomic wave functions for the initial state of both atoms. In addition, it is highly desirable to have an idea of the class of varied functions used in the direct variational method. The present work is devoted to this latter question. Just as in the theory of molecules the hydrogen molecule problem served as a touchstone for estimating the applicability of various methods, so in the theory of dispersion forces the system of two hydrogen atoms should be considered as fundamental for all subsequent calculations.

If the wave function of the ground state $\psi^{(0)} = \psi_0(r_1)\psi_0(r_2)$ has spherical symmetry in the variables r_1 and r_2, then the energy of the dipole-dipole interaction of two atoms at distance ρ may be written in the form

$$E = -\frac{6}{\rho^3} \iint \psi^{(0)} z_1 z_2 \psi^{(1)}\, dv_1 dv_2, \tag{1}$$

where the first-approximation function $\psi^{(1)}$ satisfies the differential equation

$$\{H_0(r_1) + H_0(r_2) - 2E_0\}\psi^{(1)} = \frac{z_1 z_2}{\rho^3}\psi^{(0)}, \tag{2}$$

with

$$H_0(r) = -\frac{1}{2}\Delta - \frac{1}{r}.$$

If in equation (2) one puts

$$\rho^3\psi^{(1)} = \cos\vartheta_1 \cos\vartheta_2 \psi^{(0)} \chi(r_1 r_2) \tag{3}$$

and introduces the new variables (1)

$$r_1 = \sqrt{R}\cos\alpha/2, \qquad r_2 = \sqrt{R}\sin\alpha/2, \qquad 0 \le \alpha \le \pi, \tag{4}$$

then, in the variables R and α, the equation for the function χ takes the form

$$\left\{R^2\,{}_4\Box - R^{3/2}\left(\cos\frac{\alpha}{2} + \sin\frac{\alpha}{2}\right)\frac{\partial}{\partial R} - R^{1/2}\left(\cos\frac{\alpha}{2} - \sin\frac{\alpha}{2}\right)\frac{\partial}{\partial\alpha}\right\}\chi = -\frac{R^2}{4}\sin\alpha, \tag{5}$$

where $R^2\,{}_4\Box$ denotes the operator

$$R^2\,{}_4\Box = R^2\partial^2/\partial R^2 + 3R\,\partial/\partial R + {}_4\Box_1^*, \tag{6}$$

$${}_4\Box_l^* = \frac{1}{\sin^2\alpha}\left\{\frac{\partial}{\partial\alpha}\left(\sin^2\alpha\frac{\partial}{\partial\alpha}\right) - l(l+1)\right\}.$$

The equation

$${}_4\Box_1^*\psi + (n^2-1)\psi = 0 \tag{7}$$

has a finite, single-valued, and continuous solution on the surface of the four-dimensional sphere for integer $n = 1, 2, ...$, and the eigenfunctions can be written in the form $\Phi_{n1} = P_1(\cos\vartheta)\Pi_1(n,\alpha)$, where $P_1(\cos\vartheta)$ and $\Pi_1(n,\alpha)$ are Legendre and Gegenbauer polynomials with index $l = 1$. We also note that in the case of quadrupole-quadrupole interaction the left-hand side of equation (5) would have the same form, with the only difference that in formula (6) the index $l = 1$ would have to be replaced by $l = 2$.

It would be natural to try to solve equation (5) in the form of a series containing integral and half-integral powers of R. However, it will be shown below that no such expansion exists if the coefficients of this expansion are to be finite and continuous functions on the surface of the hypersphere in four-dimensional space. The solution of equation (5) should be sought in the form of the Fock expansion [(1)]

$$\chi = \sum_{n=1,\,3/2,\,2,\ldots} R^{n-1}\sum_{k=0}^{[n-1]}(\ln R)^k\psi_{nk}, \tag{8}$$

where the symbol $[n-1]$ denotes the integer part of $(n-1)$.

If the expansion (8) is substituted into equation (5) and the coefficients of equal powers of R are set equal to zero, then for the functions ψ_{nk} one obtains a system of inhomogeneous equations which can be solved successively by the method of V. A. Fock [(1)]. The first nonzero function ψ_{nk} turns out to be the function $\psi_{2,0} = c\Pi_1(2,\alpha)$, where c is an arbitrary constant. The subsequent nonzero values of ψ_{nk} are as follows:

$$\begin{gathered}\psi_{5/2,0} = \frac{1}{2}c\sin\alpha\,(\sin\alpha/2+\cos\alpha/2),\\ \psi_{3,0} = \frac{1}{5}(c-\tfrac{1}{4})\sin\alpha + \frac{1}{8}c\sin^2\alpha;\\ \psi_{7/2,0} = \frac{1}{18}\sin\alpha\,(\sin\alpha/2+\cos\alpha/2)\,[(\tfrac{3}{10}c-\tfrac{1}{5})\sin\alpha+\tfrac{6}{5}c-\tfrac{1}{20}]\,.\end{gathered} \tag{9}$$

The equation for the function $\psi_{4,0}$ can be written in the form

$$^4\square_1^*\psi_{4,0} + 15\psi_{4,0} = -\varphi(\alpha) - 8\psi_{4,1} - 2\psi_{4,2}, \tag{10}$$

where

$$\varphi(\alpha) = \frac{1}{18}\left\{\frac{1}{20} - \frac{6}{5}c - \left(\frac{21}{5}c - \frac{11}{20}\right)\sin\alpha - \left(\frac{21}{10}c - \frac{13}{20}\right)\sin^2\alpha\right\}.$$

To obtain a finite solution, it is necessary that the right-hand side of equation (10) be orthogonal to the function $\Pi_1(4,\alpha)$. From this orthogonality condition the coefficient x of the function $\psi_{4,1} = x\Pi_1(4,\alpha)$ must be determined (the function $\psi_{4,2}$ is equal to zero). As a result we obtain the expressions for the functions $\psi_{4,0}$ and $\psi_{4,1}$

$$\psi_{4,0} = \frac{47}{19440}\sin\alpha + \sum_{n=6,\,8,\,10,\ldots}\frac{d_n}{(4^2-n^2)}\Pi_1(n,\alpha); \tag{11}$$

$$\psi_{4,1} = \frac{1}{12600\pi}\Pi_1(4,\alpha); \tag{12}$$

the coefficients d_n in (11) are

$$d_n = \frac{1}{45}\left(6c - \frac{1}{4} + \frac{42c-13}{n^2-9}\right)\frac{(-1)^{n+1}-1}{(n^2-1)^2}.$$

To the expression (11) for $\psi_{4,0}$ one may add the polynomial $c_4\Pi_1(4,\alpha)$, where c_4 is a new arbitrary constant. As for the analogous constants at the polynomials $\Pi_1(n,\alpha)$ with odd indices n, these constants may be set equal to zero, since only those functions which are symmetric with respect to the transformation $\alpha \to (\pi-\alpha)$ contribute to the integral (1).

Thus, it has been shown that logarithmic terms must be present in the expansion of the function χ. Expressions containing $(\ln R)^2$ arise in solving the equations with $n = 6$, terms $(\ln R)^3$ in the equations with $n = 8$, etc.

The arbitrary constants c_{2m} introduced above can be found from the following variational principle for the second correction

to the energy (2)

$$E(\widetilde{\psi}) = 6 \iint \left\{2\widetilde{\psi} V \psi^{(0)} + \widetilde{\psi}\left[H_0(r_1) + H_0(r_2) - 2E_0\right]\widetilde{\psi}\right\} dv_1\, dv_2 = \text{extr},$$

$$V = -z_1 z_2/\rho^3. \tag{13}$$

From the extremum condition for the functional (13) one obtains equation (2) for $\psi^{(1)}$. Thus, for example, if one confines oneself to the first term of the expansion of χ, then the van der Waals constant in the formula $E = -w/\rho^6$ is $w = 6$; when the next term of the expansion with $n = 5/2$ is taken into account, one obtains for w the value $w = 84/13 \approx 6.4615$. Calculations of the subsequent terms are carried out in an analogous way. From a practical standpoint it may prove convenient to introduce variable parameters into the functions ψ_{nk}. If, for example, the function $\psi_{3,0}$ in (9) is written in the form $\psi_{3,0} = u \sin\alpha + v \sin^2\alpha$, then we obtain $w = 6.498$; taking into account the terms with $n = 7/2$ gives $w = 6.499$, which agrees with the known result (3). The convergence, as is seen from the figures given, turns out to be very good (see also (4)).

Thus, for the dipole-dipole, quadrupole-quadrupole, and other terms of the expansion, the problem can be reduced to the study of Poisson' s equation on the surface of a four-dimensional sphere.

For those terms of the expansion for which $l_1 \neq l_2$, as, for example, occurs for the dipole-quadrupole interaction, one should turn to the Fock expansion on the surface of a six-dimensional sphere (5). For this it proves convenient to introduce the spherical coordinates considered by Morse and Feshbach (6), putting

$$r_1 = Q\cos\alpha, \qquad r_2 = Q\sin\alpha, \qquad 0 \le \alpha \le \pi/2. \tag{14}$$

In these variables the problem of the dipole-quadrupole interaction reduces to solving the equation

$$\left\{Q^2\, {}_6\Box - 2Q^2(\cos\alpha + \sin\alpha)\frac{\partial}{\partial Q} - 2Q(\cos\alpha - \sin\alpha)\frac{\partial}{\partial \alpha}\right\}\chi = -2Q^5\cos\alpha\sin^2\alpha, \tag{15}$$

where it is put that

$$Q^2\,{}_6\Box = \partial^2/\partial Q^2 + 5Q\,\partial/\partial Q + {}_6\Box^*_{12},$$

and ${}_6\Box^*_{12}$ is the operator for hyperspherical functions in six-dimensional space; the indices 1,2 refer to the values of the quantum numbers $l_1 = 1$, $l_2 = 2$. The explicit form of the eigenfunctions of ${}_6\Box^*$ is known (6).

The function χ may be sought in the form of a Fock series in powers of $Q^n(\ln Q)^k$; moreover, for even n the solution can be written in the form of linear combinations of hyperspherical functions, while for odd n the solution of the equation, just as in the four-dimensional case, can be written in the form of a definite integral through the Green' s function.

In recent years a method of calculating the van der Waals constant through the optical polarizability of atoms has become widespread (7). This method and the direct variational method described here can mutually complement each other.

It should also be noted that knowledge of the first-approximation function makes it possible to calculate not only the second but also the third correction to the energy, which may, in particular, be used in the problem of technical forces.

In conclusion I express my deep gratitude to V. A. Fock and Yu. N. Demkov for discussing the present work.

Leningrad State University
named after A. A. Zhdanov

Received
17 I 1968

REFERENCES

1. V. A. Fock, *Izv. AN SSSR, ser. fiz.*, **18**, 161 (1954).

2. H. A. Bethe, E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, Moscow, 1960.

3. L. Pauling, J. Beach, *Phys. Rev.*, **47**, 686 (1938).

4. H. R. Hasse, *Proc. Cambr. Phil. Soc.*, **27**, 66 (1931).

5. Yu. N. Demkov, A. M. Ermolaev, *ZhETF*, **36**, 896 (1959).

6. P. Morse, H. Feshbach, *Methods of Theoretical Physics*, IL, 1964.

7. A. Dalgarno, *Adv. At. Mol. Phys.*, **2**, 1 (1966).

Note: Figure translations are in progress. See original paper for figures.