Perturbation theory with allowance for exchange forces

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(Submitted April 3, 1973)
Zh. Eksp. Teor. Fiz. **65**, 926–932 (September 1973)

A perturbation theory is formulated which is applicable to interatomic interactions with allowance for exchange forces and does not require an initial orthogonal function basis. The theory is used to determine the interatomic forces and the hyperfine structure spectral line shift in a hydrogen-helium atomic mixture.

1. At present, stationary state perturbation theory, which neglects the principle of indistinguishability of identical particles, is a sufficiently well-developed and widely used theory in nonrelativistic quantum mechanics. As applied to the problem of interatomic interactions, this theory allows us to explain the van der Waals forces whose range falls in the region of fairly large interatomic distances ($R \sim 10$). In the region of smaller distances, exchange effects connected with the atomic-wave-function symmetry properties arising from the indistinguishability principle are important. At the same time, we can consider interatomic distances to be sufficiently large in the sense that interatomic interactions are weaker than intratomic forces and that perturbation theory is applicable. This region of interatomic distances is an important region in the modern physics of atomic collisions, in molecular physics, and in the theory of condensed media.

The construction of a perturbation theory in which the corrections to the wave function would at all orders be antisymmetrized with respect to permutation of the electrons meets however with a number of difficulties. First of all, if the total Hamiltonian of the atomic system under consideration is symmetric under permutation of the identical particles, then when it is split up into two parts—perturbed and unperturbed—the latter turns out to be nonsymmetric, since it is connected with a definite distribution of the numbered electrons over the atoms. When the eigenfunctions of such an unperturbed Hamiltonian are used the corrections to them turn out to be nonsymmetric.

If, on the other hand, a set of antisymmetrized unperturbed wave functions is used, then there arises difficulties connected with the necessity for the orthogonalization of the functions of this set[1]. In Ritchie's paper[2], the first of the indicated difficulties is overcome by using projection operators and symmetrizing the unperturbed Hamiltonian and the perturbation: in the construction of a series of the Brillouin-Wigner type it is assumed, however, that the antisymmetrized wave functions automatically form an orthogonal set, which, strictly speaking, is realized only in the case of infinitely large interatomic distances.

In the present paper this inconsistency is removed and a way of obtaining the corrections to a wave function in any order of perturbation theory with allowance for the Pauli principle is indicated. And, which is important, the tedious procedure of orthogonalization of the initial set is then not required.

2. Let us consider a system of two atoms—atom A and atom B—and let us denote by $R_{\text{a.u.}}$ the distance between their nuclei. Let us assume that the wave functions $\Psi_A(\{q_A\})$ and $\Psi_B(\{q_B\})$ of the isolated atoms, where the $\{q\}$ are the sets of spin and space variables for the electrons of the atoms A and B, respectively, are known, and let us construct the simple product $\Phi = \Psi_A\Psi_B$ from these functions. The wave function of the atomic system under consideration can, in the zeroth approximation (i.e., in the absence of interaction between the atoms), be obtained by applying to the function Φ the antisymmetrization operator $\hat{A}$ and allowing it to act on the electron variables of the various atoms:

$$\Psi^{(0)} = \hat{A}\Phi \equiv f\{\Psi_A(\ldots q_{Ai}\ldots)\Psi_B(\ldots q_{Bk}\ldots) - \Psi_A(\ldots q_{Ak}\ldots)\Psi_B(\ldots q_{Bi}\ldots) - \ldots\} \equiv \sum_{i=1}^{p}\Phi_i; \tag{1}$$

$\Phi_1 \equiv \Phi$, where f is a normalization vector guaranteeing the normalization condition

$$(\Psi|\Psi) = 1. \tag{2}$$

If the atom A contains r electrons and the atom B – s electrons, then the right-hand side of the expression (1) contains $p = rs + 1$ terms.

Let us further define the projection operators Λ_i according to the relations

$$\Lambda_i\Psi = \Phi_i, \quad i = 1, 2, \ldots, p. \tag{3}$$

Let us write the Hamiltonian operator $\hat{H}$ of the atomic system in the form of the following sum:

$$\hat{H} = \hat{H}_0 + \hat{V}, \tag{4}$$

where

$$\hat{H}_0 = \sum_i \hat{H}_{0i}\Lambda_i, \quad \hat{V} = \sum_i V_i\Lambda_i \tag{5}$$

are respectively the Hamiltonian operator for the unperturbed system and the perturbation operator for the system. The operator H_{01} describes the unperturbed atomic system in which a group of r electrons (with numbers 1, 2, ..., r) is located in the atom A, while the remaining group of s electrons (with numbers r + 1, r + 2, ..., r + s) is located in the atom B. The operator H_{02} corresponds to the same system, but with the k-th and *l*-th electrons in these groups interchanged, and so on. To each i-th distribution of the numbered electrons over the atoms corresponds a definite interaction operator V_i. The index a will be used to indicate the wave function and the energy level of the ground state of the system of atoms while the index b will pertain to the excited states. The wave function $\Psi_a^{(0)}$ satisfies the following equation:

$$\hat{H}_0|\Psi_a^{(0)}) = E_a^{(0)}|\Psi_a^{(0)}). \tag{6}$$

Assuming the interaction to be weak, we can represent the wave function and the ground-state energy of the system of two atoms in the form of the expansions:

$$\Psi_a = \Psi_a^{(0)} + \Psi_a^{(1)} + \ldots, \qquad E_a = E_a^{(0)} + E_a^{(1)} + \ldots \tag{7}$$

The Schrödinger equation in first-order perturbation theory has the following form:

$$\hat{H}_0|\Psi_a^{(1)})+\hat{V}|\Psi_a^{(0)})=E_a^0|\Psi_a^{(1)})+E_a^{(1)}|\Psi_a^{(0)}). \tag{8}$$

Let us apply to both sides of this equation the operator of projection unto the orthogonal complement of the subspace formed by $|\Psi_a^{(0)})$, i.e., the operator

$$P=1-|\Psi_a^{(0)})(\Phi|/(\Psi_a^{(0)}|\Phi). \tag{9}$$

Noting that $P|\Psi_a^{(0)})\equiv 0$, we obtain

$$P(\hat{H}_0-E_a^{(0)})|\Psi_a^{(1)})=-P\hat{V}|\Psi_a^{(0)}), \tag{10}$$

whence

$$\Psi_a^{(1)}=\Sigma'\frac{P|\Psi_b^{(0)})(\Phi_b|P\hat{V}|\Psi_a^{(0)})}{pf_b(E_a^{(0)}-E_b^{(0)})}, \tag{11}$$

where f_b is a normalizing factor:

$$f_b=p^{-1}(\Psi_b^{(0)}|\Phi_b)^{-1}, \tag{12}$$

and the prime on the summation sign indicates, as usual, that the summation is over the states $b \neq a$.

Subtracting the expression (9) from (10) and taking the scalar product of the difference with the vector $(\Psi_a^{(0)}|$, we obtain the first correction to the energy:

$$E_a^{(1)}=(\Psi_a^{(0)}|\hat{V}|\Psi_a^{(0)}). \tag{13}$$

That (11) is a solution to the Schrödinger equation (8) can be verified by direct substitution.

Further, $(\Psi_a^{(1)}|\Psi_a^{(0)})=0$, i.e., the normalization condition is also satisfied to first order in the perturbation. Finally, the obtained first-order corrections go over into the expressions obtained in standard perturbation theory, in which the principle of indistinguishability is neglected, i.e., when $\Psi \to \Phi$.

Let us seek the second-order correction to the wave function in the form of the sum

$$\Sigma' c_b|\Psi_b^0)(E_a^0-E_b^0)^{-1},$$

having written down beforehand the Schrödinger equation with the appropriate accuracy, and projecting the latter with the aid of the operator P unto the orthogonal complement of the subspace formed by Ψ_a^0. We successively obtain the second-order corrections to the wave function and the ground-state energy:

$$\Psi_a^{(2)}=-\frac{1}{2}|\Psi_a^0)(\Psi_a^1|\Psi_a^1)$$

$$+\sum_{b,c}{}'\frac{(\Phi_c|P(\hat{V}-E_a^1)P|\Psi_b^0)(\Phi_b|P\hat{V}|\Psi_a^0)P|\Psi_c^0)}{p^2f_bf_c(E_a^0-E_b^0)(E_a^0-E_c^0)},$$

$$E^{(2)}=\sum_b{}'\frac{(\Phi_b|P\hat{V}|\Psi_a^0)(\Psi_a^0|\hat{V}P|\Psi_b^0)}{pf_b(E_a^0-E_b^0)}. \tag{14}$$

3. As an illustration, let us consider the exchange interaction between hydrogen and helium atoms, the distance between whose nuclei is equal to R. The wave function is given by

$$\Phi=\Phi_H(\mathbf{r}_1\xi_1)\Phi_{He}(\mathbf{R}-\mathbf{r}_2;\ \mathbf{R}-\mathbf{r}_3;\ \xi_2;\ \xi_3),$$

where ξ is the spin variable and the origin has been located at the nucleus of the hydrogen atom. In the first approximation, the quantity U(R), the interaction energy of the atoms, is equal to $E_a^{(1)}$. In the one-electron approximation, the coordinate part of the helium wave function is equal to the quantity

$$\frac{\alpha^3}{\pi}\exp\{-\alpha|\mathbf{R}-\mathbf{r}_1|-\alpha|\mathbf{R}-\mathbf{r}_2|\},\quad \alpha=\frac{27}{16};$$

and the spin part corresponds to zero spin.

Further, using (5) and (13), we obtain

$$U(R)=\frac{(\Phi|V_1|\Phi)-2(\Phi|V_1|\Phi')}{1-2(\Phi|\Phi')}, \tag{15}$$

where the function Φ' differs from Φ in having the first and second electron coordinates in the perturbation (in atomic units) interchanged;

$$V_1\approx\frac{2}{R}-\frac{1}{r_2}-\frac{1}{r_3}+\frac{1}{|\mathbf{r}_1-\mathbf{r}_2|}+\frac{1}{|\mathbf{r}_1-\mathbf{r}_3|}-\frac{2}{|R-\mathbf{r}_1|}. \tag{16}$$

Upon substitution of the latter expression into (15) there arise the so-called Coulomb integrals (the first term in the numerator of (15)) and overlap or exchange integrals (the second term), which decrease exponentially with increasing distance between the atoms. These integrals have been computed in analytic form[3,4] for the hydrogen-helium system under consideration. In the region of intermediate distances ($4 < R < 6$), we can neglect the terms containing $e^{-(\alpha+1)R}$, obtaining then that approximately

$$U(R)\approx 56e^{-2R}\left(1-\frac{1.33}{R}-\frac{4}{R^2}+\frac{R-1.5}{20}\right). \tag{17}$$

The asymptotic form of the exchange interaction potential of the hydrogen atoms has the form $U_H(R) \approx -1.64R^{5/2}e^{-2R}$[5], while for the helium atoms $U_{He} \approx 8.6e^{-2.1R}$[6], so that according to Abrahamson's method, the hydrogen-helium atom interaction potential $U(R) \approx (U_H U_{He})^{1/2}$.

Estimates show that in the region of distances under consideration, the last formula and the formula (17) yield numerical values differing by not more than 10%. In the next, second-order perturbation theory (for $R \sim 10$), the interaction potential is described by the van der Waals function. The exchange corrections in the range of action of the van der Waals forces are small.

4. The region of interatomic distances under consideration here is important in connection with the problems of the physics of atomic collisions. The spectral lines of a gas are broadened and shifted as a result of atomic interactions[7]. Hydrogen buffered with helium gas is used, for example, in frequency-standard instruments. We shall restrict ourselves here to the consideration of the relative shift of the hyperfine-structure lines in such a system. Theoretical analysis of the experimental data, performed on the basis of the variational procedure[8], shows that the major portion of a line shift is, under normal conditions, due precisely to the approach of the atoms to within distances of the order of intermediate separations, i.e., exchange, and not the van der Waals, interaction is the controlling interaction. The neglect of this circumstance can lead in computations not only to incorrect magnitudes, but even to the wrong sign for the shift.

If the small orbital contribution is neglected, then the relative spectral-line shift can be found in the following manner:

$$\delta\nu=\frac{2(\Psi^0(R)|\hat{B}|\Psi_1(R))}{(\Psi^0(\infty)|\hat{B}|\Psi^0(\infty))}+\frac{f^2(R)}{f^2(\infty)}-1, \tag{18}$$

where f is the normalization factor for the ground state, the operator

$$\hat{B}=\sum_{i=1}^{3}s_{zi}\,\delta(\mathbf{r}_i),$$

and $\hat{s}_z$ is the electron spin component operator.

Substituting (11) (for the case of the hydrogen-helium system) into (18), carrying out simple transformations in which the symmetry of the operator $\hat{B}$, the definition of f, and the properties of the Dirac δ-function are taken into account, and neglecting exponentially small quantities, we obtain

$$\delta\nu = -\frac{4}{\pi}\left\{\sum_{n=2}^{\infty}\frac{n^{1/2}}{n^2-1}(\Phi_n|V_1|\Phi_a - 2\Phi_a') + \int_0^{\infty}\frac{k^{1/2}\,dk}{k^2+1}(1-e^{-2\pi/k})^{-1/2}(\Phi_k|V_1|\Phi_a - 2\Phi_a')\right\}, \tag{19}$$

where $\Phi_{n,k}$ are the simple products of the helium-atom ground-state wave function and the hydrogen-atom excited s-state wave function for the discrete and continuous parts of the spectrum, respectively. The states with nonzero orbital angular momenta make no contribution to the shift, since the corresponding wave functions vanish at the nucleus of the hydrogen atom. The last relation has been summed over the spin variables, so that the Φ in (19) is only the coordinate part of the wave function.

It is shown in the Appendix that the sum over the discrete spectrum can be replaced by integration over the continuous spectrum, so that

$$\delta\nu = -\int_0^{\infty}\frac{2k^{1/2}\,dk}{k^2+1}(1-e^{-2\pi/k})^{-1/2}\left(1+\frac{1-e^{-2\pi/k}}{1-e^{2\pi/k}}\right)[(\Phi_k|V_1|\Phi) - 2(\Phi_k'|V|\Phi)]. \tag{20}$$

In the region of interatomic distances R ~ 5, the dominant contribution to (20) is made by wave numbers k ~ 1, so that we can use in this region the asymptotic forms of the hydrogen wave functions of the continuous spectrum. Performing the integration first over k (by the method of steepest descent) and then over the coordinates, we obtain the following approximate relation:

$$\delta\nu(R) \approx \frac{-69e^{-R}}{(1+R^2)(1+R^{-1})}\left[\sin\left(\sqrt{8R}-\frac{\pi}{8}\right) - \frac{1}{R}\cos\left(\sqrt{8R}-\frac{\pi}{8}\right)\right] \tag{21}$$

The relative spectral-line shift, computed per unit pressure (Torr) and averaged over the thermal motion, is equal (see[8]) to the quantity

$$f_p = \frac{\partial}{\partial p}\overline{\delta\nu} = 0.6\cdot 10^{-7}\int_0^{\infty}\delta\nu(R)e^{-U/kT}R^2\,dR. \tag{22}$$

Substituting into this (17) and (21) and performing the integration by the method of steepest descent, we obtain (for T ≈ 300°K)

$$f_p \approx 3\cdot 10^{-9}\,\text{Torr}^{-1}.$$

For the hydrogen-helium system under consideration, the experimental value for the shift is, when adjusted to a temperature of 30°C, equal to $f_p \approx 3.4 \pm 0.2$[8]. Taking into account the approximate nature of our numerical estimates, we can evidently assert that the agreement with experiment is satisfactory.

APPENDIX

The hydrogen wave function of the continuous spectrum is proportional to the function

$$e^{-ikr}F(1+i/k;\ 2;\ 2ikr) \equiv G,$$

where F is the hypergeometric function. Let us split the function G into two parts: one having the asymptotic form of an outgoing, and the other of an ingoing spherical wave. Then the function

$$kG/(k^2+1)(1-e^{-2\pi/k}) = A + A^*, \tag{A.1}$$

where $A \sim e^{ikr}$ and $A^* \sim e^{-ikr}$ for $kr \gg 1$.

Let us consider in the complex plane of k the integral sum:

$$I = \oint_{C_1} A\,dk + \oint_{C_2} A^*\,dk, \tag{A.2}$$

where the contour C_1 consists of a semicircle of infinitely large radius located in the upper half-plane and the real axis, the pole k = 0 being circumvented from above. The contour C_2 is the complex conjugate of the contour C_1.

Since the conditions of Jordan's lemma are satisfied, the integrals along the large semicircles (as well as along the small ones) tend to zero as the radii of the semicircles tend to infinity (zero). In fact, as $|k| \to \infty$, the hypergeometric function tends to the limit[9]:

$$F(1, 2, 2ikr) \to \frac{1}{4}\left(\frac{2\pi}{ikr}\right)^{1/2} e^{ikr} J_{1/2}(kr) \sim \frac{1}{k}.$$

Therefore, the integrals along the contours are equal, on the one hand, to the integrals (in the sense of principal value) along the real axis and, on the other, to the sum of the residues of the integrand at its poles:

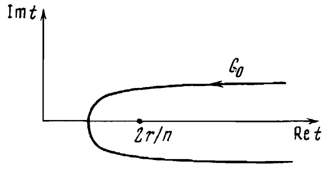
$$I = \int_{-\infty}^{\infty}(A + A^*)\,dk = 2\pi i\left[\sum_{n=2}^{\infty}\operatorname{res}(A, k = i/n) - \text{c.c.}\right]. \tag{A.3}$$

The summation in the last formula is begun at n = 2, since, as can easily be verified, the two contributions cancel each other out at the point n = 1. At the points k = 0, ±i/n for n > 2, the integrand has only simple poles.

Further, using the integral representation of the hypergeometric function[9], we obtain

$$I = \sum_{n=2}\frac{e^{r/n}}{n\pi i(n^2-1)}\int_{C_0} e^{-t}(-t)^{n-1}\left(\frac{2r}{n}-t\right)^{-n-1}dt,$$

where the contour C_0 is shown in the figure. Applying



the Cauchy formula to the obtained integral and using the well-known series representation of the hypergeometric function, we obtain

$$I = -\sum_{n=2}^{\infty}\frac{2e^{-r/n}}{n(n^2-1)}F\left(-n;\ 2;\ \frac{2r}{n}\right). \tag{A.4}$$

In virtue of the evenness of the function G(k), we can, taking (A.4) into account, transform the equality (A.3) into the following form:

$$\sum_{n=2}^{\infty}\frac{1}{n(n^2-1)}e^{-r/n}F\left(-n+1;\ 2;\ \frac{2r}{n}\right) + \int_0^{\infty}\frac{kG(k)\,dk}{k^2+1}(1-e^{-2\pi/k})^{-1}$$
$$= \frac{1}{2}\int_0 G(k)\,dk\left[1+\frac{1-e^{-2\pi/k}}{1-e^{2\pi/k}}\right]\frac{k}{(k^2+1)(1-e^{-2\pi/k})}$$

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Translated by A. K. Agyei
96