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SCATTERING OF ELECTRONS BY DIATOMIC MOLECULES IN THE APPROXIMATION OF TWO SMALL-RADIUS WELLS

R. SUBRAMANYAN[1)]

Leningrad State University

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We consider the elastic scattering of electrons by diatomic molecules in an approximation in which the potentials of interaction between the electron and the atoms are replaced by two small-radius wells. The scattering cross section is calculated in the case when the atoms have no spin, and also in the case when each atom has spin 1/2. The results of calculations are presented for the concrete case of a hydrogen molecule and are compared with experiment.

1. INTRODUCTION

THE problem of the scattering of electrons by a molecule can be reduced in a definite approximation to the problem of scattering of electrons by an electrostatic field of an immobile molecule. (For a diatomic molecule, e.g., this field has axial symmetry.) Such an approximation is valid if, on the one hand, the velocity of the electrons is not too small, so that during the time of flight the molecule does not have time to turn through a noticeable angle. From this we get that the energy should exceed 10^{-2} eV (for light molecules), see, for example,[1]. On the other hand, the energy should not exceed several eV, since we neglect the electron excitations. In such an approximation, the problem for the diatomic molecule was solved by Shimizu[2]. His calculation turn out to be quite cumbersome. Even for the simplest model, when the variables separate in elliptic coordinates, the solution cannot be obtained in explicit form.

In the present paper we use the approximation of two small-radius wells to calculate the cross section for elastic scattering of electrons by diatomic molecules. This approximation was used by Smirnov and Firsov[3] and by Demkov[4] for the problem of interaction between negative ions and atoms. For this approximation to be valid, it is necessary that the electron wavelength be much larger than the dimensions of the atoms. This condition imposes practically no additional limitations on the applicability of the method. The dependence of the binding energy of the electron on the distance between the nuclei was found in[3]. In the present paper we illustrate the application of this method to the scattering problem. The formulas obtained for the scattering cross sections are used in the concrete case of the hydrogen molecule. The obtained wave functions of the continuous spectrum can be used also for other problems (such as photodetachment etc.).

We assume that the molecule is immobile. We calculate the scattering cross section for a fixed molecule orientation, and then average it over all orientations. We likewise disregard the polarization effects. They influence the elastic scattering significantly only at small incident-electron energies, so that our result can be reasonably compared with experiment only in the interval 2–10 eV.

2. CASE OF TWO IDENTICAL SPINLESS ATOMS

The potential of interaction between the electron and the atoms of the diatomic molecule is chosen in the form of two small-radius wells. As is well known, these wells can be replaced by boundary conditions in the vicinity of each atom:

$$\Psi \sim A_i\left(\frac{1}{r_i} - c\right) + O(r_i), \qquad (1)$$

where c—parameter characterizing the depth of the well, 1/c—scattering length corresponding to the potential of the atom, and r_i—distance from the electron to the center of the i-th well.

The wave function of the electron in the field of the two small-radius wells can be written in the form

$$\Psi = \exp(i\mathbf{k}_0\mathbf{r}) + A\exp(ikr_1)/r_1 + B\exp(ikr_2)/r_2. \qquad (2)$$

where **r**—electron position, $\hbar\mathbf{k}_0$—momentum of incident electron, $k = |\mathbf{k}_0|$. The function Ψ is obviously a solution of the Schrödinger equation for the free particle

$$(\nabla^2 + k^2)\Psi = 0$$

everywhere, including the region of the wells. The coefficients A and B are determined from the boundary condition (1) near each atom. The wave function has the asymptotic form

$$\Psi \sim \exp(i\mathbf{k}_0\mathbf{r}) + F(\mathbf{k}, \mathbf{k}_0)\exp(ikr)/r,$$

where the scattering amplitude is

$$F(\mathbf{k}, \mathbf{k}_0) = \Delta_0^{-1}[\{f\exp(i\mathbf{k}_0\mathbf{R}_2) - (c + ik)\exp(i\mathbf{k}_0\mathbf{R}_1)\} \times \exp(-i\mathbf{k}\mathbf{R}_1) + \{f\exp(i\mathbf{k}_0\mathbf{R}_1) - (c + ik)\exp(i\mathbf{k}_0\mathbf{R}_2)\}\exp(-i\mathbf{k}\mathbf{R}_2)], \qquad (3)$$

$$\Delta_0 = (c + ik)^2 - f^2.$$

Here $\hbar\mathbf{k}$—momentum of scattered electron, $\mathbf{R}_1$, $\mathbf{R}_2$—positions of the two nuclei; f = exp(ikR)/R, where $R = |\mathbf{R}_1 - \mathbf{R}_2|$—distance between the nuclei. The total elastic-scattering cross section at a given molecule orientation is obtained most readily from the optical theorem. Averaging over the orientations of the molecule, we obtain ultimately the formula

$$\sigma = \frac{4\pi R^2}{K^2 D}[2(C^2 - K^2 - \cos 2K)(\sin^2 K - K^2) + (2CK - \sin 2K)^2]. \qquad (4)$$

[1)] Bhabha Center for Atomic Research, Bombay.

Here

$$D = (C^2 - K^2 - \cos 2K)^2 + (2CK - \sin 2K)^2$$

and C = cR, K = kR—dimensionless quantities.

We can also obtain readily the differential elastic scattering cross section for a given direction of the scattered electrons, by averaging $|F(\mathbf{k}, \mathbf{k}_0)|^2$ over the orientations of the molecule.

3. CASE OF ATOMS WITH SPIN 1/2

Let us consider the case when the system of the two electrons of the hydrogen molecule is in the singlet state, which corresponds to the ground state of the molecule. In this case the wave function of the scattered electrons is written in the form

$$\Psi = \{\exp(i\mathbf{k}_0\mathbf{r}) + \Phi_1(\mathbf{r})\}\chi(1,2;3) + \Phi_2(\mathbf{r})\chi(2,3;1) + \Phi_3(\mathbf{r})\chi(3,1;2), \tag{5}$$

where

$$\Phi_i(\mathbf{r}) = P_i \exp(ikr_1) / r_1 + Q_i \exp(ikr_2) / r_2, \tag{6}$$

$$\chi(i,j;k) = \frac{1}{\sqrt{2}}(\alpha_i\beta_j - \beta_i\alpha_j)\alpha_k; \tag{7}$$

α_i, β_i—spin functions of the electron i with projection ± 1/2 on the preferred direction. The functions χ satisfy the linear relation

$$\chi(1,2;3) + \chi(2,3;1) + \chi(3,1;2) = 0. \tag{8}$$

Following Smirnov and Firsov[3], we introduce new linearly independent spin functions

$$S_1 = \frac{1}{\sqrt{2}}(\alpha_3\beta_1 - \beta_3\alpha_1)\alpha_2,$$
$$T_1^- = \frac{1}{\sqrt{2}}(\alpha_3\beta_1 + \beta_3\alpha_1)\alpha_2, \qquad T_1^+ = \alpha_3\alpha_1\beta_2; \tag{9}$$

S_1 corresponds to the singlet state of the incident electron 3 and the electron of the atom 1; $T_1^\pm$ correspond to the triplet states of the same electrons. The introduction of these functions enables us to write down the boundary condition for Ψ in a convenient form.

It is easy to show that

$$\chi(2,3;1) = -\frac{1}{2}S_1 + \frac{1}{2}T_1^- - \frac{1}{\sqrt{2}}T_1^+, \qquad \chi(3,1;2) = S_1. \tag{10}$$

The wave function Ψ can be rewritten in the form

$$\Psi = \psi_1(\mathbf{r})S_1 + \psi_2(\mathbf{r})T_1^- + \psi_3(\mathbf{r})T_1^+, \tag{11}$$

where

$$\psi_i(\mathbf{r}) = A_i \exp(ikr_1) / r_1 + B_i \exp(ikr_2) / r_2 + a_i \exp(i\mathbf{k}_0\mathbf{r}), \qquad a_1 = -{}^1/_2, \quad a_2 = -{}^1/_2, \quad a_3 = 1 / \sqrt{2} \tag{12}$$

and

$$\begin{pmatrix} A_1 & B_1 \\ A_2 & B_2 \\ A_3 & B_3 \end{pmatrix} = \begin{pmatrix} -{}^1/_2 & 1 \\ {}^1/_2 & 0 \\ -1/\sqrt{2} & 0 \end{pmatrix} \begin{pmatrix} P_2' & Q_2' \\ P_3' & Q_3' \end{pmatrix}, \tag{13}$$
$$P_{2,3}' = P_{2,3} - P_1, \quad Q_{2,3}' = Q_{2,3} - Q_1.$$

Near the atom 1 each term of the right side of expression (11) is an eigenfunction of the Hamiltonian (see[3]). The spatial parts of $\psi_i(\mathbf{r})$ should therefore satisfy the following boundary conditions near the atom 1:

$$\psi_1(\mathbf{r}) \sim A_1(1 / r_1 - c_s), \quad \psi^2(\mathbf{r}) \sim A_2(1 / r_1 - c_i), \quad \psi_3(\mathbf{r}) \sim A_3(1 / r_1 - c_t), \tag{14}$$

where c_s^{-1} and c_t^{-1} are the scattering lengths corresponding to the singlet and triplet states.

From these three boundary conditions we obtain only two linearly independent linear homogeneous equations for the determination of P_2', Q_2', P_3', and Q_3'. Introducing the spin functions S_2, T_2^-, and T_2^+ in analogy with the functions S_1, T_1^- and T_1^+, and repeating all the manipulations for the atom 2, we obtain two more equations. We thus have the system of equations

$$\begin{pmatrix} c_1 & f & -2c_1 & -2f \\ c_2 & f & 0 & 0 \\ 2f & 2c_1 & -f & -c_1 \\ 0 & 0 & f & c_2 \end{pmatrix} \begin{pmatrix} P_2' \\ Q_2' \\ P_3' \\ Q_3' \end{pmatrix} = \begin{pmatrix} -\exp(i\mathbf{k}_0\mathbf{R}_1) \\ \exp(i\mathbf{k}_0\mathbf{R}_1) \\ \exp(i\mathbf{k}_0\mathbf{R}_2) \\ \exp(i\mathbf{k}_0\mathbf{R}_2) \end{pmatrix}, \tag{15}$$

where $c_{1,2} = c_{s,t} + ik$. Equating to zero the determinant of the matrix of the left side and replacing k by $i\alpha$, we obtain the equation of Smirnov and Firsov[3] for the determination of the bound (and quasistationary) states in the case of identical atoms.

At large values of r, the wave function (5) has the asymptotic form

$$\Psi \sim \{\exp(i\mathbf{k}_0\mathbf{r}) + F_1(\mathbf{k}, \mathbf{k}_0)\}\chi(1,2;3) + F_2(\mathbf{k}, \mathbf{k}_0)\chi', \tag{16}$$

where

$$\chi' = \chi(2,3;1) - \chi(3,1;2)$$

is a spin function orthogonal to $\chi(1,2;3)$; the scattering amplitudes $F_{1,2}(\mathbf{k}, \mathbf{k}_0)$ are given by

$$F_{1,2}(\mathbf{k}, \mathbf{k}_0) = \mp\frac{1}{2}[(P_2' \pm P_3')\exp(-i\mathbf{k}_0\mathbf{R}_1) + (Q_2' \pm Q_3')\exp(-i\mathbf{k}_0\mathbf{R}_2)]. \tag{17}$$

The total elastic-scattering cross section at a given molecule orientation is given by the optical theorem

$$\sigma(\mathbf{k}_0) = \frac{4\pi}{k}\,\mathrm{Im}\,F_1(\mathbf{k}_0, \mathbf{k}_0). \tag{18}$$

Substituting the solution of (15) in (18) we obtain after a few algebraic manipulations

$$\sigma(\mathbf{k}_0) = \frac{4\pi}{k}(f_1 + \cos(\mathbf{k}_0\mathbf{R})f_2), \tag{19}$$

where

$$f_1 = \mathrm{Im}(M / \Delta), \qquad f_2 = \mathrm{Im}(N / \Delta). \tag{20}$$

Here

$$\begin{aligned} \Delta &= -4f^4 + f^2(c_1^2 + 6c_1c_2 + c_2^2) - 4c_1^2c_2^2, \\ M &= 6c_1^2c_2 + 2c_1c_2^2 - 2f^2c_1 - 6f^2c_2, \\ N &= 8f^3 + fc_2^2 - 3fc_1^2 - 6fc_1c_2. \end{aligned} \tag{21}$$

Averaging over the orientations of the molecule in (19) gives the effective elastic-scattering cross section

$$\sigma = \frac{4\pi}{k}\left(f_1 + \frac{\sin kR}{kR}f_2\right). \tag{22}$$

4. DISCUSSION

The formulas obtained above can be used, for example, for the concrete problem of the scattering of electrons by a hydrogen molecule. The main question which arises here is how to choose the parameters c, c_s, and c_t for the given molecule. If we disregard the spin, we can assume that the scattering length for each well is equal to the scattering length for the static potential of the hydrogen atom, i.e., $c^{-1} = 9.44a_0$ (see[5]). The distance between the wells R is assumed to be $1.4a_0$, i.e., the real distance between the nuclei in the H_2 molecules. The results for the effective cross section are shown in

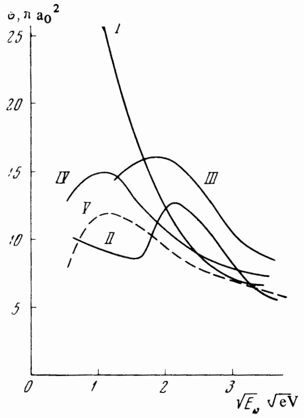

FIG. 1. Cross section for elastic scattering of electrons by the hydrogen molecule (E—energy of incident electrons).

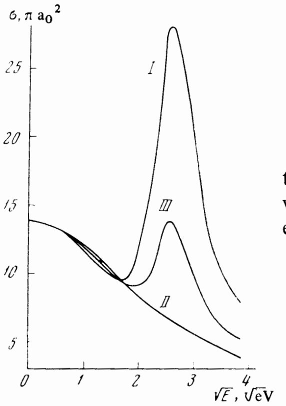

FIG. 2. Cross section for elastic scattering of electrons by two small-radius wells at cR = 0.5 (E—energy of incident electrons).

Fig. 1, curve 1. At zero incident-electron energy, the cross section tends to the value $43.5\pi a_0^2$. It should be noted that with such a choice of the constant c, the system consisting of two small-radius wells has a bound state which is missing from the real H_2 system. This state is the result of the fact that we have neglected exchange. It corresponds, as it were, to states in the atom, forbidden by the Pauli principle, within the framework of the Hartree method.

It is interesting that by choosing the value of the constant c we can readily consider a case when there is a quasistationary state with relatively large lifetime $\hbar/\Gamma$. For this problem, the transition of the bound states into quasistationary ones was considered by Demkov in[6]. (In the general case such a transition was investigated by Demkov and Drukarev[7].) The same paper gives the trajectories of the poles of the S-matrix for the symmetrical and asymmetrical cases. Resonance is possible only for the antisymmetrical case. Thus, for example, a sharp resonant maximum in scattering is obtained at a positive value of the constant c. Figure 2 shows the curves for the scattering cross section at cR = 0.5. Curve I shows here the scattering cross section for electrons, when the molecule is oriented parallel to the direction of incidence of the electrons; curve II—when the orientation of the molecule is perpendicular to the direction of incidence of the electrons; curve III shows the cross section averaged over the molecule orientations.

Curve II on Fig. 1 shows the results of a calculation with allowance for exchange (formula (22)). For the singlet and triplet scattering lengths, the mean values $a_+ = 5.97\, a_0$ and $a_- = 1.77\, a_0$, respectively, were used, as obtained by Schwartz[8] by a variational method for the problem of electron scattering by a hydrogen atom. We could use also other values of these parameters, for example, those calculated from the experimentally obtained potential curves for H_2^- and H_2. Curves III and IV show the experimental results obtained by the Ramsauer method[9] and by the electron cloud method; curve V shows the theoretical results obtained by Massey and Ridley[10] with allowance for exchange (these curves are given also in[5]).

As seen from the figures, the approximation of two small-radius wells give fair results at medium incident-electron energies. The main advantage of the model, however, lies in the fact that it can be readily generalized to the case of more complicated two-atom and polyatomic molecules, and in particular, to molecules with unlike atoms. It should be noted that this is the only two-center problem of scattering theory, known to us, which can be solved exactly.

The scattering of neutrons by the hydrogen molecule was considered earlier[11] in the approximation of two small-radius wells, the nuclei being replaced by the wells. However, owing to the small effective radius of the nuclear forces, in that problem the multiple scattering can be neglected. In our case the cross section for scattering by one well is comparable with the square of the distance between them. It is therefore necessary to take into account multiple scattering, and this was actually done in the solution of the problem.

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[1] K. Takayanagi and S. Geltman, Phys. Rev. **138**, A1002 (1965).

[2] M. Shimizu, J. Phys. Soc. Japan **18**, 811 (1963).

[3] B. M. Smirnov and O. B. Firsov, Zh. Eksp. Teor. Fiz. **47**, 232 (1964) [Sov. Phys.-JETP **20**, 156 (1965)].

[4] Yu. N. Demkov, ibid. **46**, 1126 (1964) [**19**, 762 (1964)].

[5] B. L. Moiseiwitsch, Atomic and Molecular Processes (Russ. Transl.), Mir, 1964.

[6] Yu. N. Demkov, Zh. Eksp. Teor. Fiz. **49**, 885 (1965) [Sov. Phys.-JETP **22**, 615 (1966)].

[7] Yu. N. Demkov and G. F. Drukarev, ibid. **49**, 691 (1965) [**22**, 479 (1966)].

[8] C. Schwartz, Phys. Rev. **124**, 1468 (1961).

[9] C. Ramsauer and R. Kollath, Ann. Physik **12**, 529 (1932).

[10] H. S. W. Massey and R. O. Ridley, Proc. Phys. Soc. **A69**, 659 (1956).

[11] J. Schwinger and E. Teller, Phys. Rev. **52**, 286 (1937).

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