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## Electron Capture by Polar Molecules\*

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It is shown that binding of electrons in the electric dipole field of polar molecules cannot possibly occur, if the molecules have an electric dipole moment smaller than the critical value  $D_0 = 1.63 \times 10^{-18}$  esu cm, irrespective of the size of the dipole. This result casts doubts on a proposed mechanism of electron scattering by polar molecules, namely, electron capture with rotational excitation of the molecule.

### I. INTRODUCTION

THE scattering of low-energy electrons by molecules has been shown experimentally to present peculiar features when the molecules possess a permanent electric dipole moment.<sup>1</sup> The interaction between the charge of the electron and the dipole moment of the molecule gives rise to a long-distance force which significantly modifies the scattering process. The cross section for this process has been calculated for the case of a point-dipole scatterer by Altshuler<sup>2</sup> in the first Born approximation, and exactly by Mittleman and von Holdt.<sup>3</sup>

However, the experimental results for some polar molecules do not agree with the theory. Turner<sup>4</sup> has tried to explain the discrepancy by taking into account the possibility of temporary capture of the electron with rotational excitation of the molecule. This mechanism can lead to the desired increase of the theoretical cross section, at least for molecules with a high enough dipole moment and a sufficiently low moment of inertia.

But the question of the possibility of electron capture has remained unsettled up to now. Indeed, one has to examine whether or not a dipole field of arbitrary strength can possess bound states. We will show that

only polar molecules with a dipole moment higher than a certain critical value can capture electrons. We first prove this result in the case of a point dipole. (Mittleman and von Holdt<sup>3</sup> quoted it without proof.) But this is a rather unphysical case in that the bound states, when they exist, have an infinite binding energy. We then show that exactly the same critical moment exists in the physical situation of a finite dipole, irrespective of the size of the dipole. Finally, we comment on the physical implications of this result which will be seen to cast doubt on the validity of Turner's explanation.

### II. THE POINT-DIPOLE CASE

Let  $e$  and  $\mu$  stand for the charge and mass of the electron, respectively, and  $D$  for the dipole moment of the molecule, supposed to be point-like. The Schrödinger equation for the wave function of the electron is written

$$\left( -\frac{\hbar^2}{2\mu} \Delta + e \frac{\mathbf{D} \cdot \mathbf{r}}{r^3} - E \right) \Psi = 0. \quad (1)$$

Let us define a "dimensionless dipole moment"  $\alpha$ :

$$\alpha = \frac{2\mu e D}{\hbar^2} = 2 \frac{D}{ea_0} \quad \text{or} \quad D = \alpha \times 1.27 \times 10^{-18} \text{ esu cm}, \quad (2)$$

where  $a_0$  is the Bohr radius.

Equation (1) is separable in spherical coordinates. Choosing the  $z$  axis along the dipole moment, and putting

$$\Psi(r, \theta, \varphi) = \frac{1}{r} R(r) \Theta(\theta) e^{im\varphi}, \quad (3)$$

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<sup>1</sup> G. S. Hurst, L. B. O'Kelly, and J. A. Stockdale, *Nature* **195**, 66 (1962); G. S. Hurst, J. A. Stockdale, and L. B. O'Kelly, *J. Chem. Phys.* **38**, 2572 (1963).

<sup>2</sup> S. Altshuler, *Phys. Rev.* **107**, 114 (1957).

<sup>3</sup> M. H. Mittleman and R. E. von Holdt, *Phys. Rev.* **140**, A726 (1965).

<sup>4</sup> J. E. Turner, *Phys. Rev.* **141**, 21 (1966).

where we have already taken advantage of the rotation symmetry around the  $z$  axis, we obtain the two equations

$$\left(-\frac{d^2}{dr^2} + \frac{C}{r^2} - 2\mu E\right)R=0, \quad (4)$$

and

$$\left[-\frac{1}{\sin\theta} \frac{d}{d\theta} \left(\sin\theta \frac{d}{d\theta}\right) + \frac{m^2}{\sin^2\theta} + \alpha \cos\theta - C\right]\Theta=0. \quad (5)$$

$C$  is the separation constant, and  $m$  an integer.

The radial equation (4), which determines the energy levels once  $C$  has been computed from Eq. (5), is the same as the one for a central potential  $C/r^2$ . This singular potential is known to have no bound states at all if  $C > -\frac{1}{4}$ , and bound states with infinite negative energies if  $C < -\frac{1}{4}$ .<sup>5</sup> In the latter case, this phenomenon of "fall towards the center" is due to the strong singularity of the potential and will not occur for a finite dipole. The problem is thus reduced to seeing whether Eq. (5) allows for separation constants  $C < -\frac{1}{4}$ . But in Eq. (5),  $C$  appears as the eigenvalue of an operator  $K$  which is the sum of the ordinary square of the angular momentum  $\mathbf{L}^2$  and of the operator  $\alpha \cos\theta$ :

$$K = \mathbf{L}^2 + \alpha \cos\theta.$$

Both  $\mathbf{L}^2$  and  $\alpha \cos\theta$  are operators which are bounded from below, by 0 and  $-\alpha$ , respectively, so that  $K$  itself is certainly bounded from below. Its lowest eigenvalue  $C_0$  thus obeys

$$C_0 \geq -\alpha.$$

As a consequence, in order to have bound states, one must have  $C_0 < -\frac{1}{4}$ , which requires  $\alpha > \frac{1}{4}$ . This proves the *existence* of a critical dipole moment  $\alpha_0$  obeying

$$\alpha_0 > \frac{1}{4}.$$

But one can actually compute  $\alpha_0$ . We start by noticing the presence of the positive term  $m^2/\sin^2\theta$  in the operator  $K$ , which implies that the lowest eigenvalue  $C_0$  of  $K$  certainly will be found in the subspace  $m=0$ . Let us then investigate Eq. (5) in the  $m=0$  case. We look for its solutions as sums of Legendre polynomials:

$$\Theta(\theta) = \sum_{l=0}^{\infty} d_l P_l(\cos\theta). \quad (6)$$

Equation (5) is equivalent to the following three-term recursion relations to be obeyed by the coefficients  $d_l$ 's:

$$\alpha \frac{l}{2l-1} d_{l-1} + [l(l+1) - C] d_l + \alpha \frac{l+1}{2l+3} d_{l+1} = 0. \quad l=0, 1, \dots \quad (7)$$

<sup>5</sup> See, for instance, L. D. Landau and E. M. Lifschitz, *Quantum Mechanics* (Pergamon Press Inc., London, 1958), Sec. 35.

According to a standard method,<sup>6</sup> the set of all these recursion relations can be transformed into a continued fraction expansion for the eigenvalue  $C$  in terms of itself and the parameter  $\alpha$ . In the present case we obtain

$$C = -\frac{\alpha^2}{3(2-C)} - \frac{4\alpha^2}{5(6-C)} - \dots - \frac{k^2\alpha^2}{(2k+1)[k(k+1)-C]} - \dots \quad (8)$$

This is an implicit equation determining  $C$  as a function of  $\alpha$ . It has a discrete infinity of solutions which we already know for  $\alpha=0$ :

$$C_l(\alpha=0) = l(l+1), \quad l=0, 1, 2, \dots$$

The various functions  $C_l(\alpha)$  can be obtained from Eq. (8) as power expansions in  $\alpha^2$ , putting

$$C_l(\alpha) = l(l+1) + c_1^l \alpha^2 + c_2^l \alpha^4 + \dots$$

and identifying the power expansions in  $\alpha^2$  of both sides of the Eq. (8). We are only interested in the lowest eigenvalue which is computed as

$$C_0(\alpha) = -\frac{\alpha^2}{6} + \frac{11}{30} \left(\frac{\alpha^2}{6}\right)^2 - \frac{133}{450} \left(\frac{\alpha^2}{6}\right)^3 + \dots \quad (9)$$

The number of terms computed is quite sufficient for determining the critical value  $\alpha_0$  of the dipole moment, which is the solution of the equation

$$C_0(\alpha_0) = -\frac{1}{4}.$$

A numerical calculation yields

$$\alpha_0 = 1.28 \dots, \quad (10)$$

corresponding to an electric dipole moment

$$D_0 = 1.63 \times 10^{-18} \text{ esu cm.} \quad (11)$$

This value of  $\alpha_0$  agrees with the one quoted by Mittleman and von Holdt.<sup>3</sup> It can be compared with the approximate value computed by Fox and Turner<sup>7</sup> using the WKB method:

$$D_0^{\text{WKB}} = 2.19 \times 10^{-18} \text{ esu cm}$$

and has been closely approached by the latter authors<sup>8</sup> using a variational method:

$$D_0^{\text{var}} = 1.65 \times 10^{-18} \text{ esu cm.}$$

We have thus shown that no bound states can exist in a point-dipole field if the dipole moment is smaller than the critical value  $D_0$ .

<sup>6</sup> See, for instance, P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Sec. 5.2.

<sup>7</sup> K. Fox and J. E. Turner, *Am. J. Phys.* **34**, 606 (1966).

<sup>8</sup> K. Fox and J. E. Turner, *J. Chem. Phys.* **45**, 1142 (1966).

## III. THE EXTENDED-DIPOLE CASE

The electron now moves in the combined electric field of two opposite charges  $Q$  and  $-Q$ , separated by a distance  $2R$ . Calling  $r_1$  and  $r_2$ , respectively, the distances from the electron to the two charges, we write the Schrödinger equation

$$\left(-\frac{\hbar^2}{2\mu}\Delta + \frac{eQ}{r_1} - \frac{eQ}{r_2} - E\right)\Psi = 0. \quad (12)$$

This equation is separable in prolate confocal coordinates, defined by

$$\xi = \frac{r_1 + r_2}{2R}, \quad (1 \leq \xi)$$

$$\eta = \frac{r_1 - r_2}{2R}, \quad (1 \geq |\eta|).$$

As usual,  $\varphi$  will denote the azimuthal angle about the axis of the fixed charges.

We further define a dimensionless energy parameter  $\epsilon$ :

$$\epsilon = \frac{2\mu R^2 E}{\hbar^2}, \quad (14)$$

and a dimensionless dipole moment  $\alpha$ , as previously:

$$\alpha = \frac{2\mu e D}{\hbar^2} = \frac{4\mu e Q R}{\hbar^2}. \quad (15)$$

Writing the wave function in the separated form

$$\Psi(\xi, \eta, \varphi) = X(\xi)Y(\eta)e^{im\varphi}, \quad (16)$$

we obtain the two equations

$$\left[\frac{d}{d\xi}(\xi^2 - 1)\frac{d}{d\xi} - \frac{m^2}{\xi^2 - 1} + \epsilon\xi^2 - C\right]X = 0, \quad (17)$$

and

$$\left[-\frac{d}{d\eta}(1 - \eta^2)\frac{d}{d\eta} + \frac{m^2}{1 - \eta^2} + \epsilon\eta^2 + \alpha\eta - C\right]Y = 0, \quad (18)$$

where  $C$  is the separation constant and  $m$  an integer. We remark that the solutions of these equations only depend on the two dimensionless parameters  $\alpha$  and  $\epsilon$ . In fact, no other independent dimensionless parameter can be formed out of the quantities  $eQ$ ,  $\mu$ ,  $\hbar$ ,  $R$ ,  $E$ .

The crucial fact now is that once the dipole moment  $D$  (or its dimensionless expression  $\alpha$ ) is fixed, the size  $R$  of the dipole only shows up as a scale factor for the energy, according to (14). Then, if for a given value of  $\alpha$ , the equations (17)–(18) admit a series of bound states  $\epsilon_n$ ; the corresponding physical binding energies

$$E_n = \frac{\hbar^2}{2\mu R^2} \epsilon_n$$

TABLE I. Values of the electric dipole moments for various molecules as compared to the critical value.

	H <sub>2</sub> S	HCl	NH <sub>3</sub>	Critical value	H <sub>2</sub> O	D <sub>2</sub> O	HF	H <sub>2</sub> O <sub>2</sub>
$D \times 10^{18}$ (in esu cm)	0.92	1.07	1.47	1.63	1.85	1.86	1.91	2.13
$\alpha$	0.72	0.84	1.16	1.28	1.46	1.47	1.51	1.68

will all tend to minus infinity when the size  $R$  of the dipole goes to zero.

In other words, for each value  $\alpha$  such that the extended dipole potential possesses bound states, the point-dipole potential must exhibit the phenomenon of "fall towards the center," i.e., infinitely low-lying bound states. But in the limit  $R \rightarrow 0$  we have to recover the results obtained in the preceding section for a point dipole, that is, no bound states at all for a dipole moment below the critical value. The inescapable conclusion then is that the critical value  $D_0(11)$  is critical for an extended dipole as well, irrespective of its size. Below this value, there cannot exist any bound state.

It is gratifying that numerical computations of energy levels in a finite-dipole field are completely compatible with the existence of this critical moment.<sup>9</sup> Because of the poor convergence of the expansions used, these calculations have not been pushed below a value of the dipole moment  $\alpha \approx 1.7$ , but in this region the binding energies decrease very rapidly with decreasing  $\alpha$ .

We could now try to compute explicitly the values of the binding energies in that unknown region just above the critical value. However, these energies prove to be quite small. Indeed, already for the value  $\alpha \approx 1.7$  or  $D = 2.14 \times 10^{-18}$  esu cm, the smallest for which calculations have been done, the ground state has a binding energy as small as  $6.3 \times 10^{-4}$  eV.

In view of this smallness, as compared typically to molecular rotational excitations of, say,  $10^{-2}$ – $10^{-1}$  eV, we do not feel it worthwhile to investigate the exact behavior of the binding energies as they go to zero with the dipole moment tending to its critical value.

## IV. DISCUSSION

It has been proposed by Turner<sup>4</sup> that temporary capture of the electron with rotational excitation of the molecule could account for the peculiarities observed in the scattering of electrons by some polar molecules.<sup>1</sup> Such a mechanism, if allowed, would be most efficient for molecules with a low enough moment of inertia, so that their rotational energy levels have spacings small compared to the thermal energies of the electrons.

Besides the molecules H<sub>2</sub>O, D<sub>2</sub>O, and H<sub>2</sub>S for which the experiments have shown the mentioned discrepancies with simple scattering theories, Turner suggests

<sup>9</sup> R. F. Wallis, R. Hermann, and H. Milnes, J. Mol. Spectry, 4, 51 (1960).

that  $\text{NH}_3$ , HF, HCl, and  $\text{H}_2\text{O}_2$  should exhibit the same behavior. Table I gives the electric dipole moments of these molecules as well as the critical moment (11). Of course, neither of these molecules produces an electric field identical to the one of an extended dipole. Nevertheless, the fact that the same critical value holds for a point dipole and for a finite dipole, leads one to the conclusion that this critical value is quite insensitive to the higher order multipole components of the electric field, and essentially depends on the dipole moment. A critical value very close to  $D_0$ , as computed here, certainly holds for any type of polar molecule.

It is seen in Table I that  $\text{H}_2\text{S}$ , HCl, and  $\text{NH}_3$  have dipole moments below the critical value, whereas the moments of  $\text{H}_2\text{O}$ ,  $\text{D}_2\text{O}$ , HF, and  $\text{H}_2\text{O}_2$  lie above this value.<sup>10</sup> The former molecules thus cannot bind electrons in their dipole fields and electron capture cannot

<sup>10</sup> Mittleman and von Holdt (Ref. 3) in their Fig. 3 attribute a subcritical moment to  $\text{H}_2\text{O}$ . This is due to their omission of a factor 2 when converting from the  $D$ 's to the dimensionless  $\alpha$ 's.

occur for them. This is especially significant for the molecule  $\text{H}_2\text{S}$ , which has been shown to have an anomalous electron scattering cross section.

We are thus led to question seriously the role of electron capture in the scattering of low-energy electrons by polar molecules. At least, this mechanism cannot operate universally, and further investigations clearly are necessary to explain the enhanced cross sections observed for some polar molecules.

*Note added in proof.* After the present paper was submitted to this journal, the same problem was independently solved by three other groups of workers. M. H. Mittleman and V. P. Myerscough [Phys. Letters **23**, 545 (1966)] and J. E. Turner and K. Fox [Phys. Letters **23**, 547 (1966)] use rather complicated methods, while W. B. Brown and R. E. Roberts [J. Chem. Phys. (to be published)] use the same method as ours and show that the presence of a repulsive radial core will not modify the value of the critical dipole moment.

## Single- and Double-Quantum Photodetachment of Negative Ions\*

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The recent measurement of the transition probability for the double-quantum detachment of an electron from  $\text{I}^-$  has prompted a new theoretical study of this problem. A central-field model for bound and free states is used, in which a parameter is adjusted in the potential to yield the observed binding energies of the negative ions. An implicit-sum method, requiring the solution of inhomogeneous radial equations, is used to evaluate the sums over intermediate states. The results for  $\text{I}^-$  lie almost within the experimental uncertainty. The cross sections for single-quantum photodetachment and electron elastic scattering (from the neutral atom) are also given for the ions studied:  $\text{C}^-$ ,  $\text{O}^-$ ,  $\text{F}^-$ ,  $\text{Si}^-$ ,  $\text{S}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ .

### I. INTRODUCTION

**I**N a recent experiment, Hall, Robinson, and Branscomb<sup>1</sup> measured the transition probability ( $W_2$ ) for the double-quantum photodetachment of an electron from  $\text{I}^-$  at the ruby-laser wavelength. Their result is higher by a factor of 3 to 6 (considering the experimental uncertainty) than a theoretical estimate made by Geltman.<sup>2</sup> The latter theoretical estimate was based on the approximation that all the continuum states of

the negative ion may be represented by plane waves. This approximation makes trivial the summation over allowed intermediate states (which all lie in the continuum), and yields an expression for  $W_2$  which is simply proportional to  $\sigma_1$ , the cross section for single-quantum photodetachment. This latter cross section is well known experimentally for  $\text{I}^-$  (Ref. 3), as well as for a number of other negative ions. The present work is an attempt to improve upon the plane-wave approximation by treating one-electron continuum states exactly in an assumed central field.

The interaction Hamiltonian between the radiation field and an atomic electron is

$$H' = -\frac{e}{mc^2} \mathbf{p} \cdot \mathbf{A}(0) + \frac{e^2}{2mc^2} A^2(0), \quad (1)$$

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<sup>1</sup> J. L. Hall, E. J. Robinson, and L. M. Branscomb, Phys. Rev. Letters **14**, 1013 (1965).

<sup>2</sup> S. Geltman, Phys. Letters **4**, 168 (1963); **19**, 616 (1965).

<sup>3</sup> B. Steiner, M. L. Seman, and L. M. Branscomb, J. Chem. Phys. **37**, 1200 (1962).