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Dissociation of Molecular Ions by Electric and Magnetic Fields*†

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A general discussion of the dissociation of diatomic molecules and molecular ions by electric fields is presented. These calculations pertain primarily to the ground electronic states of the molecular systems. The H_2^+ ion is treated in considerable detail; the required fields for the dissociation range from 10^5 v/cm for the uppermost vibrational state to 2×10^8 v/cm for the ground state. The many-electron homonuclear ions are treated in successive charge states. The HD^+, HT^+, HD, LiH^+, and LiH^{++} heteronuclear ions are considered. The dissociation of homonuclear ions and heteronuclear ions exhibit distinctly different features. The HD^+ and HT^+ ions are more susceptible to discussion than is H_2^+. The extent to which the dissociation by an electrostatic field and by the Lorentz force, $e\mathbf{v}\times\mathbf{B}$, are equivalent is considered. The rates of induced dipole transitions to lower vibrational states can be made negligibly small compared with the dissociation rates. The application of this work to particle accelerators and to the injection problem for fusion devices is discussed.

I. INTRODUCTION

IF an atomic or molecular system is placed in a steady electric field, the Coulomb binding forces are supplemented by an additional force which tends to separate the charges. One would expect that a sufficiently intense external electric field would lead to a dissociation of the system. Oppenheimer calculated this effect for a hydrogen atom in its ground state and found that the instability of the atom was inappreciable for field intensities much less than 10^8 volts per centimeter (v/cm).[1] These calculations have been extended to various excited states of the hydrogen atom by Lanczos.[2]

In this paper we consider the electric dissociation of the general diatomic molecule or molecular ion in its ground electronic state. The dissociation of a molecular system exhibits distinctive features compared with the atomic case. The nature of this difference for the two cases is a consequence of the fact that the only mode of dissociation available to the atom leads to a transition of the electron into a free state. For the molecule, however, there is an infinite number of possible final states leading to dissociation, corresponding to the successive bonding and antibonding electronic states of the system.

One might expect that a loosely bound ion in which one of the uppermost vibrational states of a particular electronic state is occupied would provide an example of a system that would dissociate in an appreciably smaller field than is required for atomic dissociation. Such an excited vibrational level is found here to be susceptible to a mode of dissociation in which the molecular system divides into two atomic systems, a form of predissociation induced by the electric field. Detection of the electric dissociation of the successive vibrational states would provide a means for studying directly the vibrational levels of molecular ions.[2a]

Aside from its general physical interest, such a mechanism may have application in the particle-accelerator field and to the injection problem for fusion experiments. A process for changing the charge state of an atomic or molecular system which utilized the action of the Lorentz force has application as an injection method for fusion devices that have large magnetic fields. Such change-of-charge-state mechanisms for trapping energetic particles inside a magnetic field region have previously been proposed utilizing conventional ionization processes.[3,4] It is common practice in many cyclotron establishments to accelerate H_2^+ ions as a source of protons. As cyclotron energies are increased, it is of interest to inquire into the stability of successive vibrational states. The work presented here should be useful as a basis for estimating these successive stabilities.

These considerations had prompted a study of the dissociation of the simplest molecular structure, the hydrogen molecular ion.[5] In a first approximation to the dissociation by a magnetic field, the problem was replaced by the simpler one of the dissociation by a purely electrostatic field, in the belief that the solution of this latter problem would exhibit the basic features of the dissociation by the Lorentz force.[6] Here we extend this earlier paper to calculate the electric fields necessary to dissociate the successive vibrational levels of H_2^+. The extension of this problem to the many-electron

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[1] J. Robert Oppenheimer, Phys. Rev. **31**, 66 (1928).

[2] C. Lanczos, Z. Physik. **62**, 518 (1930); **65**, 431 (1930); **68**, 204 (1931).

[2a] *Note added in proof.* Predissociation of H_2^+ ions induced by an electrostatic field has been observed by A. C. Riviere and D. R. Sweetman, Phys. Rev. Letters **5**, 560 (1960).

[3] E. J. Lauer, University of California Radiation Laboratory Report UCRL-4554, 1955 (unpublished).

[4] J. Luce, Conference on Controlled Thermonuclear Reaction, Princeton University, October 17–20, 1955; Atomic Energy Commission Report TID-7503, 1956 (unpublished), 335.

[5] J. R. Hiskes and J. L. Uretsky, University of California Radiation Laboratory Report UCRL-8255, 1958 (unpublished).

[6] Dr. W. I. Linlor (Hughes Research Laboratory) has informed the author of his own independent interest in the electric dissociation of H_2^+.

system and to heteronuclear molecules has been facilitated by the recent work of Dalgarno and McCarroll,[7] and that of Cohen, Judd, and Riddell.[8]

II. THE GENERAL EQUATIONS

A. Separation of the Motions

In this section we discuss the Hamiltonian for a general many-electron diatomic molecule moving in an electrostatic field. The development given here follows closely that of Dalgarno and McCarroll, and of Cohen, Judd, and Riddell. Insofar as is convenient, we adopt the notation of the latter.

Consider an n-electron diatomic molecule with nuclei of masses M_a and M_b and charges ea and eb in the presence of an electrostatic field. Let $\mathbf{r}_a$, $\mathbf{r}_b$, and $\mathbf{r}_{ei}$ represent the coordinates of the two nuclei and the ith electron, respectively, all measured with respect to the laboratory system. Take the direction of the z axis along the electric field. The Schrödinger equation for this system is written

$$-\frac{\hbar^2}{2}\left\{\frac{1}{M_a}\nabla_a{}^2+\frac{1}{M_b}\nabla_b{}^2+\frac{1}{m}\sum_{i=1}^{u}\nabla_{ei}{}^2\right\}\psi +\{V_1+V_2\}\psi=E\psi;\quad -\frac{\hbar}{i}\frac{\partial}{\partial t}\psi=E\psi, \tag{II.1a}$$

where V_1 is the sum of all the Coulomb terms and

$$V_2=-e\mathcal{E}\left[az_a+bz_b-\sum_{i=1}^{n}z_{ei}\right]. \tag{II.1b}$$

The center-of-mass motion can be separated from the equation for the internal motions by introducing $n+2$ new variables—a center-of-mass coordinate $\mathbf{r}_c$, a relative nuclear coordinate $\mathbf{r}_n$, and n additional coordinates $\mathbf{r}_i$, measuring the distance of the ith electron from the center of mass of the two nuclei. The resulting equation for the center of mass describes the motion of a particle of mass (M_a+M_b+nm) and charge $e(a+b-n)$ moving in an electrostatic field.[9]

The equation for the internal motions becomes

$$-\frac{\hbar^2}{2}\left\{\frac{1}{M_n}\nabla_n{}^2+\frac{1}{M_a+M_b}\sum_i^n\sum_{j\neq i}\boldsymbol{\nabla}_i\cdot\boldsymbol{\nabla}_j+\frac{1}{m_e}\sum_i^n\nabla_i{}^2\right\}\psi +\left\{V_1-e\mathcal{E}\left[\frac{aM_b-bM_a}{M_a+M_b}\right]z_n +e\mathcal{E}\left[1+\frac{(a+b-n)m}{M_a+M_b+nm}\right]\sum_i^n z_i\right\}\psi=W\psi, \tag{II.2}$$

with

$$M_n=M_aM_b/(M_a+M_b),$$

and

$$m_e=m(M_a+M_b)/(M_a+M_b+m),$$

and where V represents the mutual Coulomb interactions between the nuclei and electrons and expressed in terms of the relative coordinates.

In the interest of separating the relative nuclear motion from the electronic motions, we proceed by assuming a solution of the form

$$\psi(\mathbf{r}_n,\mathbf{r}_i)=\textstyle\sum_K\psi_K(\mathbf{r}_n,\mathbf{r}_i)\chi_K(\mathbf{r}_n).$$

Inserting this expansion into Eq. (II.2), multiplying by $\psi_\lambda{}^*$, and integrating over all electronic coordinates, we have

$$-\frac{\hbar^2}{2M_n}\nabla_n{}^2\chi_\lambda +\left[\frac{abe^2}{r_n}-e\mathcal{E}\left(\frac{aM_b-bM_a}{M_a+M_b}\right)z_n+E_\lambda(r_n)-w\right]\chi_\lambda+\theta_{\lambda K} +\sum_K\chi_K\int\psi_\lambda{}^*\left\{-\frac{\hbar^2}{2m_e}\sum_{i=1}^n\nabla_i{}^2+V_e +e\mathcal{E}\left[1+\frac{(a+b-n)m}{M_a+M_b+nm}\right]\sum_{i=1}^n z_i-E_\lambda(r_n)\right\} \times\psi_K d^3r_1\cdots d^3r_n, \tag{II.3}$$

where $\theta_{\lambda K}$ is an infinite series of terms coupling the electronic and nuclear motions,[7,8] and V_e is the Coulomb potential describing the interactions of the electrons moving in the field of the nuclei.

The electronic functions ψ_K are defined by setting the bracketed quantity in the integrand of Eq. (II.3) to zero. The remaining terms serve to define the nuclear motion. In a first approximation to the nuclear motion, it is customary to set the $\theta_{\lambda K}$ series to zero. The various vibrational states belonging to a particular electronic state, E_λ, are then determined by the equation

$$-\frac{\hbar^2}{2M_n}\nabla_n{}^2\chi_\lambda +\left[\frac{abe^2}{r_n}-e\mathcal{E}\frac{aM_b-bM_a}{M_a+M_b}z_n+E_\lambda(r_n)-W\right]\chi_\lambda=0. \tag{II.4}$$

For homonuclear molecules, the $\theta_{\lambda K}$ series is a simple correction to the nuclear potential, the leading term in this series contributing a quantity of order m/M_n.[8] For the heteronuclear one-electron problem in lowest order, there is a degeneracy at large r_n for the two distinguishable cases in which the electron is associated with either mass a or mass b. It has been shown that in this latter case, in addition to providing a correction to the poten-

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[7] A. Dalgarno and R. McCarroll, Proc. Roy. Soc. (London) **A237**, 383 (1956).

[8] S. Cohen, D. L. Judd, and R. J. Riddell, Phys. Rev. **119**, 384 (1960).

[9] J. R. Hiskes, University of California Radiation Laboratory Report UCRL-9182, 1960 (unpublished).

tial, the leading terms in $\theta_{\lambda K}$ also provide a means for removing the degeneracy that exists at large r_n. The motion is now determined by a set of coupled equations, and the notion of a potential is no longer appropriate.[8] In this discussion we shall usually neglect the effects of these higher-order corrections, since the primary effect of the electric field is already pronounced in lowest order; the use of a potential in describing the effects of the electric field for both the homonuclear and heteronuclear cases is then valid.

B. Vibrational Transitions

1. Spontaneous Emission

Here we are concerned with vibrational transitions between the various vibrational states belonging to the ground electronic state of the molecule. The lifetimes of these states can play an essential part in the interpretation of various experiments involving molecular processes. There have been conflicting statements in the literature regarding these vibrational transitions, particularly with respect to quadrupole transitions in homonuclear molecules.

In reference 9, the spontaneous-transition rate for dipole transitions is shown to be

$$\frac{1}{T_d}=\frac{4}{3}\frac{e^2}{c^3}\frac{V_{kj}{}^3}{\hbar}\left[\frac{aM_b-bM_a}{M_a+M_b}\right]^2|(\chi_k|\mathbf{r}_n|\chi_j)|^2.$$

In the case of homonuclear molecules, the dipole transition rate is identically zero. As an example of these transition rates for heteronuclear molecules, consider the HD$^+$ ion for which we have $\hbar V_{10}\approx 0.22$ ev and $r_n\approx 2a_0$. The lifetime of this first excited state is approximately 200 microseconds (μsec). For the uppermost states, the lifetimes will be about two orders of magnitude longer than for this lowest transition. Since the time of flight of an ion in an electrostatic accelerator is some tens of microseconds, we conclude that for the purposes of many experiments these states are sufficiently long-lived to be considered stable.

For homonuclear molecules, the quadrupole transition rate is given by

$$\frac{1}{T_Q}=\frac{4}{3}\frac{e^2}{c^3}\frac{V_{kj}{}^3}{\hbar}\left(\frac{a}{2}\right)^2|(\chi_k|\mathbf{r}_n(\mathbf{k}\cdot\mathbf{r}_n)|\chi_j)|^2.$$

These quadrupole lifetimes are approximately a factor of $(2\lambda/ar_n)^2$ longer than are the dipole lifetimes.

2. Induced Transitions

The presence of the electric field has the effect of inducing vibrational transitions. One is generally concerned with the rate of these induced transitions compared with the dissociation rate. In reference 9 it is shown that the induced transition rate is given approximately by

$$\frac{1}{T_I}=\frac{4}{3}\frac{e^4}{c^3}\frac{V_{kj}\mathcal{E}^2}{\hbar^3}|(\psi_2\chi_k|r_1r_n\cos\theta_n|\psi_1\chi_j)|^2.$$

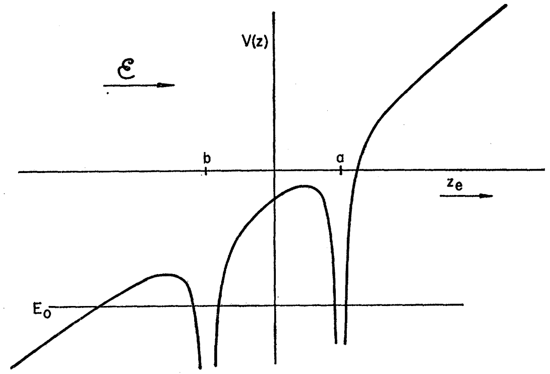

FIG. 1. The electronic potential for a diatomic molecule in the presence of an electric field and for some particular internuclear separation. This potential is exact for a one-electron system and is schematically correct for the many-electron case.

The transition rate given in reference 5 is in error. The selection rules for these transitions have been discussed previously by Condon.[10]

This transition rate exhibits a simple power dependence on the electric field value. The dissociation rate, on the other hand, is exponentially dependent on the field value. For any particular level, therefore, it is possible to choose a field value for which the over-all transition rate will exceed the dissociation rate, and vice versa.

III. APPLICATIONS

A. Homonuclear Molecules

Having derived the general equations in the preceding section, we shall now apply these results to several particular molecular ions. In any discussion of the theory of diatomic molecules, the symmetry features of homonuclear molecules lead to a clear distinction between the properties of homonuclear and heteronuclear molecules. This distinction becomes even more evident in a treatment of the dissociation by electric fields. Accordingly, we shall divide the problem at this point and consider first the dissociation of homonuclear molecules.

For homonuclear molecules, we have $a=b$ and $M_a=M_b$; the coefficient of z_n in Eq. (II.3) vanishes and there is no explicit dependence on $\mathcal{E}$ appearing in the equation for the nuclear motion. We shall see, however, that an implicit dependence on $\mathcal{E}$ is contained in the electronic eigenvalue, $E_\lambda(r_n)$.

1. Dissociation of $H_2{}^+$

The simplest molecule and the one for which an exact treatment of dissociation can be given is the

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[10] E. U. Condon, Phys. Rev. **41**, 759 (1932).

hydrogen molecular ion. We begin the discussion by considering the electronic equation for this one-electron system:

$$\left\{\frac{-\hbar^2}{2m_e}\nabla_1{}^2-\left[\frac{e^2}{|\mathbf{r}_1-\frac{1}{2}\mathbf{r}_n|}+\frac{e^2}{|\mathbf{r}_2+\frac{1}{2}\mathbf{r}_n|}-\epsilon\mathcal{E}z_1\right]\right\}\psi_K$$

$$=E_K(r_n)\psi_K, \quad \text{(III.1)}$$

where $\epsilon=[1+m/(2M+m)]e$.

The potential function seen by the electron is illustrated in Fig. 1 for the case in which the two nuclei are oriented along the field direction and for some particular internuclear separation. It is clear from the figure that the electron may leak out toward the left, away from the region of the two protons. This would correspond to a complete dissociation of the system, i.e., dissociation into a free electron and two free protons. Although this represents a possible mode of dissociation, it is not the primary mode. Rather, the primary effect of the term $\epsilon\mathcal{E}z_1$ is to perturb the electronic eigenvalues. This perturbation in turn leads to a disruption of the nuclear motion.

Equation (III.1) for $\mathcal{E}=0$ is separable in confocal elliptic coordinates ξ, η, ϕ. These coordinates are defined by

$$\xi\equiv(r_a+r_b)/r_n, \quad \eta\equiv(r_b-r_a)/r_n,$$

where r_a and r_b measure the distances of the electron from proton a and proton b, respectively.

On introduction of these coordinates into Eq. (III.1), there result three separated equations—one elementary, the other two requiring numerical integration for their general solution.[11–13] These integrations have also been carried out by Bates, Ledsham, and Stewart for several electronic states; the results are tabulated over a range $0\leqslant r_n/a_0\leqslant 10$.[14]

Another set of functions has been given by Cohen, Judd, and Riddell,[8] using a variational calculation in confocal elliptic coordinates. Their variational functions are of the form

$$\psi_1=A_1\cosh[\tfrac{1}{2}q_1(r_n)\eta r_n]\exp[-\tfrac{1}{2}p_1(r_n)\xi r_n],$$

and

$$\psi_2=A_2(\xi)\sinh[\tfrac{1}{2}q_2(r_n)\eta r_n]\exp[-\tfrac{1}{2}p_2(r_n)\xi r_n]. \quad \text{(III.2)}$$

Here the variational parameters $p(r_n)$ and $q(r_n)$ are tabulated for the interval $0\leqslant r_n/a_0\leqslant 20$.

Consider now the effect of the term $\epsilon\mathcal{E}z_1$ on the unperturbed electronic states. For large internuclear separations, the bonding and antibonding states ψ_1 and ψ_2 are degenerate; a perturbation treatment of the term $\epsilon\mathcal{E}z_1$, though adequate for small internuclear separations, loses its validity for large internuclear separations. This degeneracy of ψ_1 and ψ_2 for large internuclear separation suggests that in a first approximation we consider diagonalizing the Hamiltonian (III.1) but retaining only the submatrix formed from these two electronic states.

For the evaluation of H_{12} we must first transform the term $\epsilon\mathcal{E}z_1$ into the x'', y'', and z'' system oriented with respect to the internuclear axis. Introducing Eulerian angles λ and μ, we have

$$\epsilon\mathcal{E}z_1=\epsilon\mathcal{E}[x_1''\sin\lambda+y_1''\sin\mu\cos\lambda+z_1''\cos\mu\cos\lambda].$$

The functions (III.2) are independent of ϕ, and the terms in x'' and y'' vanish under the ϕ integration. Noting that $\cos\mu\cos\lambda=\cos\theta_n$, where θ_n is the angle between the internuclear axis and the electric-field direction, the relevant perturbation is then

$$\epsilon\mathcal{E}z_1=\epsilon\mathcal{E}z_1''\cos\theta_n.$$

In the evaluation of H_{12} using the functions given in Eq. (II.2), the relevant perturbation expressed in confocal elliptic coordinates is written.

$$\epsilon\mathcal{E}z_1=\tfrac{1}{2}\epsilon\mathcal{E}r_n\eta_1\xi_1\cos\theta_n.$$

The matrix elements are given by

$$H_{11}=E_1, \quad H_{22}=E_2,$$

and

$$H_{12}=H_{21}=\tfrac{1}{8}\pi\epsilon\mathcal{E}(\cos\theta_n)A_1A_2r_n{}^4[E_3D_1-E_1D_3].$$

The additional terms that appear in the H_{11} and H_{22} matrix elements,

$$\tfrac{1}{8}\pi\epsilon\mathcal{E}(\cos\theta_n)A_1{}^2r_n{}^4[E_{31}C_1-E_{11}C_3],$$

and

$$\tfrac{1}{8}\pi\epsilon\mathcal{E}(\cos\theta_n)A_2{}^2r_n{}^4[E_{32}F_1-E_{12}F_3],$$

respectively, are each identically zero, In the limit as

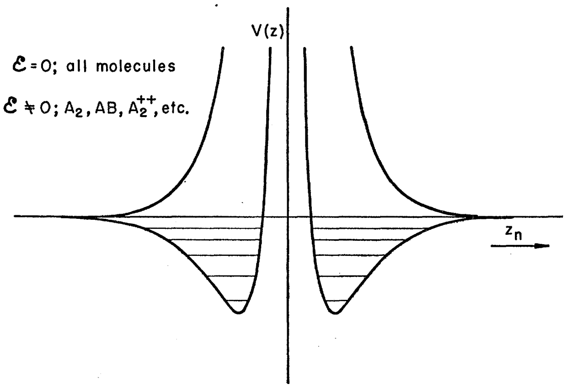

FIG. 2. The nuclear potential for a diatomic molecular system in the absence of an electric field. The vibrational states are indicated schematically by the light horizontal lines. In the presence of an electric field this potential remains unperturbed in lowest order for heteronuclear molecules and homonuclear systems in even charge states.

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[11] O. Burrau, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. 7, 1 (1927).

[12] E. Teller, Z. Physik 61, 458 (1930).

[13] E. A. Hyllerass, Z. Physik 71, 739 (1931).

[14] D. R. Bates, K. Ledsham, and A. L. Stewart, Phil. Trans. Roy. Soc. London, Ser. A, 246, 215 (1934–4).

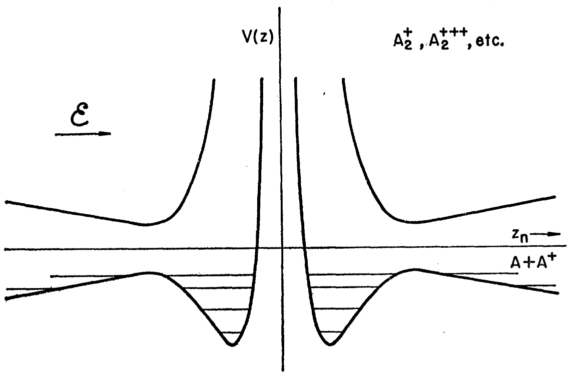

FIG. 3. The nuclear potential for a homonuclear ion in an odd-charge state in the presence of an electric field. The asymptotic potential for the lower electronic state falls off as $-\frac{1}{2}\epsilon\mathcal{E}|z_n|$.

$r_n \to \infty$, we have $H_{12} \to \frac{1}{2}\epsilon\mathcal{E}r_n\cos\theta_n$. The integrals B, C, D, E, and F are defined in the appendix.

With these matrix elements, diagonalization yields two new electronic states, ψ_g and ψ_μ, whose eigenvalues are, respectively,

$$E_{g,\mu} = \tfrac{1}{2}(E_1+E_2) \mp \tfrac{1}{2}(E_2-E_1)[1+4H_{12}^2/(E_2-E_1)^2]^{\frac{1}{2}}. \qquad \text{(III.3a)}$$

For large values of r_n, these reduce to

$$E_g = E_1 - \tfrac{1}{2}\epsilon\mathcal{E}r_n|\cos\theta_n|,$$

and

$$E_u = E_2 + \tfrac{1}{2}\epsilon\mathcal{E}r_n|\cos\theta_n|. \qquad \text{(III.3b)}$$

In Fig. 2 is shown the unperturbed nuclear potential for the two lowest electronic states. Figure 3 indicates the distortion of the nuclear potentials in the presence of the electric field; the potentials are drawn along the electric-field direction. The symmetry of the potential about the origin follows as a necessary consequence of the variance of the Hamiltonian (II.3) for a homonuclear molecule under inversion of the nuclear coordinates. From this figure it is clear that as the electric field increases, the nuclear potential deforms until the uppermost vibrational state becomes unstable. The ion will then dissociate into a free proton and a hydrogen atom according to $H_2^+ \to H + p$. This mode of dissociation is a special form of predissociation.

At first glance, the symmetric potential of Fig. 3 might conflict with one's intuitive feeling that the potential of either electronic state should fall off approximately monotonically from left to right. This point can be clarified by examining the new electronic wave functions appropriate to the diagonalized Hamiltonian. For the perturbed electronic states, one finds

$$\psi_g = [(E_g-E_2)^2+H_{12}^2]^{-\frac{1}{2}}\{(E_g-E_2)\psi_1+H_{12}\psi_2\}, \qquad \text{(III.4a)}$$

and

$$\psi_u = [(E_g-E_2)^2+H_{12}^2]^{-\frac{1}{2}}\{-H_{12}\psi_1+(E_g-E_2)\psi_2\}.$$

Consider the limit as r_n becomes large and the nuclear axis is aligned along the electric field, corresponding to proton a lying in the direction of the electric field with respect to proton b. We have

$$\psi_g \to \pi^{-\frac{1}{2}}e^{-r_b}, \quad \psi_u \to \pi^{-\frac{1}{2}}e^{-r_a}. \qquad \text{(III.4b)}$$

Equations (III.4b) are to be interpreted as meaning that in this limit of large internuclear separation, the ground electronic state is one in which the electron is associated with proton b and proton a is free, and the excited electronic state is one in which the electron is associated with proton a and proton b is free. For the lower electronic state, this corresponds to moving the positively charged proton a in the positive field direction, hence lowering the potential. For the excited electronic state, the positively charged proton b is moved against the field direction, thus raising the potential. Upon rotating the internuclear axis 180° with respect to the electric field, a similar argument shows that the electron becomes associated with proton a and proton b is free. The variation of the potential illustrated in Fig. 3 is then understood.

The higher-order effects which were neglected in diagonalization can be estimated by using perturbation theory and taking as the basis functions the two solutions of Eq. (III.4a) together with all the unperturbed higher-state functions. In the limit as r_n goes to zero, the molecular ion degenerates into a He^+ ion in its $1S$ state. The Stark shift for this state is

$$\Delta E = -(9/64)a_0^3\mathcal{E}^2.$$

In the limit of large internuclear separation, the electronic state is that of a hydrogen atom in a $1S$ state. The Stark shift for this state is

$$\Delta E = -(9/4)a_0^3\mathcal{E}^2.$$

For the range of electric-field values of interest for dissociating the upper vibrational states, these higher-order corrections are negligible. For dissociating the lowest vibrational states, these corrections, though not negligible, are not too significant. Their effect on the transition rate is comparable to ignoring them completely and increasing the electric field value some 5 to 10%.

The potential function for the nuclear motions has been determined, and we consider the nuclear dissociation. The equation for the nuclear motion is given by

$$\{-(\hbar^2/2M_n)\nabla_n^2+(e^2rn) + E_g(r_n,\theta_n,\mathcal{E}) - W_{1v}\}X_{1v} = 0. \qquad \text{(III.5a)}$$

The subscript v is introduced to distinguish the various vibrational states belonging to the lowest electronic state. In the limit of large internuclear separation, the asymptotic form of this equation is

$$\{-(\hbar^2/2M_n)\nabla_n^2+E_1(r_n) - \tfrac{1}{2}\epsilon\mathcal{E}r_n|\cos\theta_n| - W_{1v}\}X_{1v} = 0. \qquad \text{(III.5b)}$$

In the asymptotic region, the $E_1(r_n)$ is constant and can be absorbed in the W_{1v}.

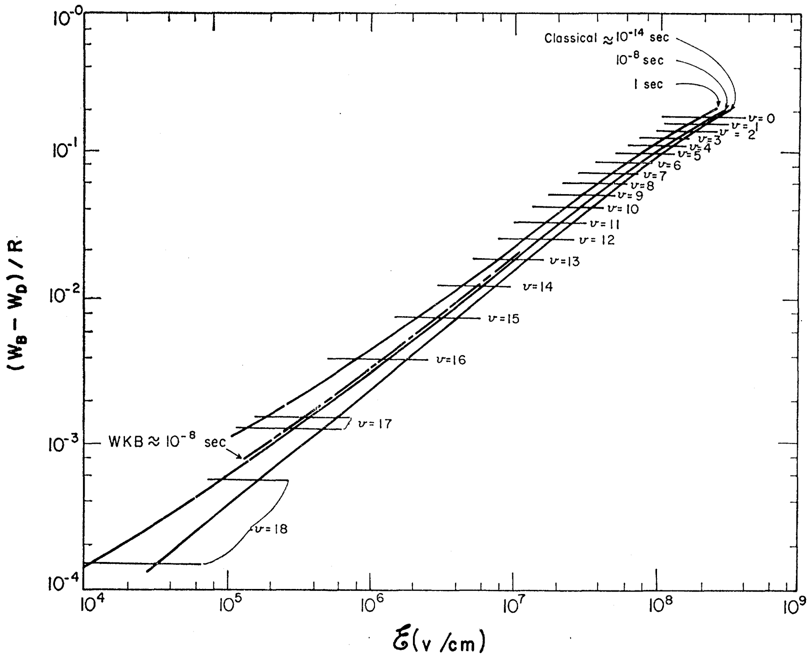

FIG. 4. Binding energy measured from the unperturbed dissociation limit vs electric field for the various vibrational states of the H_2^+ ion and for $J=0$. The intersection of the horizontal line with the curve marked "classical" determines the electric field necessary to dissociate the ion in 10^{-14} sec. The diagonal lines marked 10^{-8} sec and 1 sec determine the fields necessary for dissociation in these times, respectively. The two horizontal lines for $v=18$ and $v=17$ indicate the range of uncertainty in these calculations. The results of the WKB calculations are also indicated.

It is clear from Fig. 3 that if the maxima of the potential lie above an eigenvalue, the proton may leak away from the region of the hydrogen atom. This effect of barrier penetration is not negligible. To treat the nuclear dissociation taking into account these effects of barrier penetration, we have used Oppenheimer's formula for the transition rate.[1] Using the exact bound-state wave functions,[15,16] the electric fields necessary for dissociating the ion in 1 sec and in 10^{-8} sec have been calculated for the nonrotating molecule, that is,

$$J=m=0.$$

The results of these calculations are summarized in Fig. 4, which is a plot of binding energies, expressed in Rydberg units, of the bound vibrational states against the electric field value. The intersection of the horizontal lines with the sloping lines marked 1 sec and 10^{-8} sec determines the electric-field values necessary to dissociate the ion in these times. Included on these graphs is a curve marked "classical," which would give the field necessary for dissociation in the absence of barrier penetration. For this case, the ion would dissociate in a time comparable to its classical vibration period, i.e., 10^{-14} sec.

The electric field gives rise to a first-order perturbation that has the effect of lowering the unperturbed vibrational states prior to dissociation. If we use the curve labeled "classical" to determine the electric-field value, the first-order perturbation of the various vibrational states has been calculated and plotted in Fig. 5. These perturbed eigenvalues have been used in the calculations summarized in Fig. 4.

The calculations of the vibrational eigenvalues of the unperturbed molecular ion are uncertain by perhaps as much as 0.005 ev. The range of this uncertainty for the two upper states is indicated in Fig. 4 by plotting two horizontal lines for each of these upper states.

The transition rate given above is based on the final-state eigenfunctions, which ignore the bonding molecular potential. This rate is such as to lead to an overestimate of the field required to dissociate the ion in a particular time. An underestimate of the required field can be made by assuming the perturbed potential to be spherically symmetric and using a one-dimensional WKB barrier-penetration formula. The calculations for dissociation in 10^{-8} sec using this formula are indicated in Fig. 4 by the dashed curve. The discrepancy between these two calculations together with the uncertainty in the unperturbed eigenvalues provides a basis for estimating the over-all errors in these calculations.

The calculations summarized in Fig. 4 refer to the transition rates of nonrotating ($J=0$) molecular ions. In the more general case the effects of rotation must be considered. As an illustration of the significance of these rotational effects, let us compare the fields required for dissociation in 10^{-8} sec for an ion in the $v=15$ vibrational state and for the rotational states $J=4$, $m=0,4$, with the fields required for dissociating an ion in the same vibrational state but in a $J=0$ rotational state. For $m=0$, the electric field necessary for dissociation is approximately 30% less for $J=4$ than for $J=0$. For $J=4$, $m=4$, the required dissociation field is approximately 40% larger than $J=0$. We conclude that the presence of rotation has the effect of lowering the thresh-

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[15] S. Cohen, J. R. Hiskes, and R. J. Riddell, University of California Laboratory Report UCRL-8871, 1959 (unpublished).

[16] S. Cohen, J. R. Hiskes, and R. J. Riddell, Phys. Rev. **119**, 1025 (1950).

old fields necessary for dissociating a particular vibrational level.

2. *Dissociation of Many-Electron Systems*

Turning our attention to the many-electron problem, we find relatively little quantitative information in the literature on potential functions for many-electron molecular ions. Only for the He_2^+ ion and the Li_2^+ ion has there been any attempt to calculate the ground-state-potential functions, and here the emphasis has been primarily on determining equilibrium internuclear separations and potential minima.[17–19] Accordingly, our treatment of these many-electron ions cannot be as precise as for the one-electron systems, and quantitative estimates of the fields necessary for dissociation will have to be made largely on the basis of extrapolating the properties of the corresponding neutral molecules.

The many-electron problem is treated by using the molecular-orbital approximation. In this approximation, the many-electron molecular system is constructed by filling the successive two-centered orbitals of the hydrogen molecular ion. In its most primitive form, the interaction between the electrons is ignored, and the molecule is constructed by using the unperturbed ground-state and excited-state orbitals. For this work we shall require only that the orbitals possess the proper symmetry features and have the correct asymptotic form. The wave function for the entire system is to be expressed in determinantal form.

For the evaluation of the matrix elements, we have recourse to standard theorems on matrix elements between determinantal wave functions.[20] The general form of the perturbation with which we shall be concerned occurs in the electronic Eq. (II.5) and has the form

$$R=\epsilon\mathcal{E}\left[1+\frac{(a+b-n)m}{M_a+M_b+nm}\right]\sum_i^n z_i=\tfrac{1}{2}\epsilon\mathcal{E}r_n\cos\theta_n\sum_{i=1}^n \eta_i\xi_i.$$

Let ψ_i represent a determinantal function describing the ith electronic state, and a_k a particular spin orbital in ψ_i. We have then

$$(\psi_j|R|\psi_i)=0,$$

if ψ_j and ψ_i differ by more than one set of quantum numbers, and

$$(\psi_j|R|\psi_i)=\pm\int a_k^*(1)R(1)a_l(1)d^3r_1, \quad \text{(III.6a)}$$

where the values of a_k and a_l differ by no more than their spin functions or their orbital quantum numbers. For diagonal elements we have

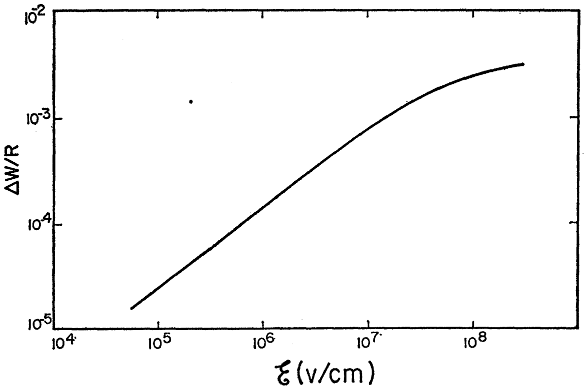

FIG. 5. First-order perturbation vs electric field for the various vibrational states of the H_2^+ ion. The perturbation for each vibrational level has been calculated using for the electric field the value given by the curve labeled "classical" in Fig. 4.

$$(\psi_j|R|\psi_j)=\sum_{i=1}^n\int a_i^*(1)R(1)a_i(1)d^3r_1. \quad \text{(III.6b)}$$

We shall also use the first of Hund's rules to determine the lowest state of several possible spin states. According to this rule, we choose the maximum value of spin consistent with the Pauli principle. These theorems and rules are adequate for a general discussion of the many-electron problem.

(*a*) *The H_2 molecule.* For the ground state, the lowest orbital is occupied by two electrons with spins opposed to give a ${}^1\Sigma_g{}^+$ state. The wave function for this ground state is given by

$$\psi_g=\mathcal{A}\psi_1(1)\alpha(1)\psi_1(2)\beta(2).$$

Here $\mathcal{A}$ is an antisymmetrizing operator, the α's and β's are the conventional spin functions, and the ψ_1 function is of the form given in Eq. (III.2). Asymptotically this electronic state goes into $H_2\rightarrow H+H$.

For the first excited state, which asymptotically is degenerate with the ground state, the ground-state orbital ψ_1 and the first excited orbital ψ_2 are each occupied. Hund's rule calls for a spin-one state. The wave function for the ${}^3\Sigma_u{}^+$ antibonding state is given by

$$\psi_g=\mathcal{A}\psi_1(1)\alpha(1)\psi_2(2)\alpha(2).$$

Following the procedure for H_2^+, we again diagonalize the appropriate 2-by-2 submatrix. The matrix elements are now

$$H_{11}=(\psi_g|\tfrac{1}{2}e\mathcal{E}r_n\cos\theta_n(\eta_1\xi_1+\eta_2\xi_2)|\psi_g)+E_1=0+E_1=E_1,$$
$$H_{22}=(\psi_u|\tfrac{1}{2}e\mathcal{E}r_n\cos\theta_n(\eta_1\xi_1+\eta_2\xi_2)|\psi_u)+E_2=0+E_2=E_2,$$

and

$$H_{12}=H_{21}=(\psi_u|\tfrac{1}{2}e\mathcal{E}r_n\cos\theta_n[\eta_1\xi_1+\eta_2\xi_2]|\psi_g)=0.$$

For homonuclear molecules, the diagonal terms will always be unperturbed, since the perturbation is an odd function. The H_{12} term vanishes because of both the

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[17] S. Weinbaum, J. Chem. Phys. **3**, 547 (1935).

[18] H. M. James, J. Chem. Phys. **3**, 9 (1935).

[19] E. A. Mason and J. T. Vanderslice, J. Chem. Phys. **29**, 361 (1958).

[20] E. U. Condon and G. H. Shortely, *The Theory of Atomic Spectra* (Cambridge University Press, New York, 1935), pp. 169–171.

orthogonality of the spin functions and the cancellation of the orbital integrals. This result could have been obtained immediately by noting that ψ_2 and ψ_1 differ by two sets of quantum numbers and invoking the first of Eq. (III.6a). The ground state and first excited state of H_2 are therefore unperturbed in this approximation. The asymptotic potential in the presence of the field is illustrated in Fig. 2; predissociation of the H_2 molecule will therefore not occur. For the H_2 molecule, the mode of dissociation is one in which an electron is stripped off, as is suggested in Fig. 1.

The above argument for H_2 is readily generalized to any neutral homonuclear molecule that has a $^1\Sigma_g^+$ ground state, corresponding to a molecule with closed shell orbitals. The first excited state will be occupied by one electron which, according to Hund's rule, will couple its spin with the last electron in the unfilled orbital to give a spin-one state. Using the first part of Eq. (III.6a), we have our result. For those molecules that do not have a $^1\Sigma_g^+$ ground state, similar arguments together with successive Hund's rules lead to the same conclusion.

(*b*) *Dissociation of singly ionized molecules.* In the limit of large internuclear separation, the ground electronic state of a general singly ionized molecule A_2^+ goes over into a state consisting of a neutral atom and a singly ionized atom, according to $A_2^+ \rightarrow A + A^+$. The molecular ion will have an odd number of electrons, with the last electron unpaired in its respective orbital. The first excited state will consist of a state in which the unpaired electron occupies the next-higher orbital. However, since it remains unpaired, Hund's rule is inapplicable, and our result is given by the second part of Eq. (III.6a). This matrix element is always nonzero, since $a_k^{(1)}$ and $a_l^{(1)}$ will have different spatial symmetries. The result is analogous to the H_2^+ case illustrated in Fig. 3, with the asymptotic potential varying as $-\frac{1}{2}\epsilon\mathcal{E}r_n|\cos\theta_n|$.

(*c*) *Dissociation of doubly ionized molecules.* The ground electronic state of the doubly ionized molecule dissociates according to $A_2^{++} \rightarrow A^+ + A^+$. For these molecular ions, the argument is similar to that for the neutral molecules. The first excited state contains an electron in the next-higher orbital which couples its spin with the remaining unpaired electron such that the first theorem of Eq. (III.6a) applies. The asymptotic potential is unperturbed as in Fig. 2.

We conclude this section with the general observation that, for a homonuclear molecule with an even charge state, predissociation will not occur, and the ground electronic state is as illustrated in Fig. 2. In the case of an odd charge state, predissociation will occur, and the electronic states are as illustrated in Fig. 3, with the potential falling off asymptotically as $-\frac{1}{2}\epsilon\mathcal{E}r_n|\cos\theta_n|$.

B. Heteronuclear Molecules

For heteronuclear molecular ions, the invariance of the Hamiltonian (II.3) under inversion of the nuclear coordinates is no longer a restraint on the problem. As a consequence, the dissociation of heteronuclear molecules exhibits essentially distinct features compared with the homonuclear case. The nuclear potential is now affected both by the implicit dependence on $\mathcal{E}$ contained in the electronic eigenvalue and the explicit term

$$-e\mathcal{E}[(aM_b-bM_a)/(M_a+M_b)]z_n$$

contained in the nuclear Eq. (II.4).

1. Dissociation of HD⁺

We begin the discussion by considering the one-electron HD^+ system. In the general discussion of the heteronuclear problem, we shall take M_a to be the mass of the lighter nucleus and M_b to be the mass of the heavier nucleus. Before considering the analytic form of the electronic wave functions, we note that the origin of the electronic coordinate system has been taken at the center of mass of the two nuclei, whereas the origin of the confocal elliptic coordinate system is taken at the center of the two nuclei. For the heteronuclear case, the Eulerian transformation λ, μ must be followed by a translation along the internuclear axis.

The Eulerian transformation λ, μ of the perturbation $\epsilon\mathcal{E}z_1$ into the x', y', z' system oriented along the internuclear axis is given by

$$\epsilon\mathcal{E}z_1=\epsilon\mathcal{E}[x_1' \sin\lambda+y_1' \sin\mu \cos\lambda+z_1' \cos\mu \cos\lambda].$$

If z_0 is the position of the center of mass with respect to the origin of the x'', y'', z'' system, we have

$$z_0=(r_n/2)[(M_a-M_b)/(M_a+M_b)].$$

The perturbation in the x'', y'', z'' frame is then

$$z_1=e\mathcal{E}[x_1'' \sin\lambda+y_1'' \sin\mu \cos\lambda+(z''-z_0) \cos\lambda \cos\mu].$$

The terms in x'' and y'' will vanish under the ϕ integration as before. Our relevant perturbation term expressed in the η, ξ, ϕ coordinates is now written as

$$\epsilon\mathcal{E}z_1=\tfrac{1}{2}\epsilon\mathcal{E}r_n \cos\theta_n[\eta_1\xi_1-(M_a-M_b)/(M_a+M_b)].$$

In the limit of large internuclear separation, the ground electronic state of the unperturbed HD^+ ion goes over into a state in which the electron is associated with the deuteron, and the first excited state goes over into a state in which the electron is associated with the proton. The appropriate wave functions are given, respectively, by[8]

$$\psi_b=A_b[\cosh(Q_1\eta/2)e^{-P_1\xi/2} \\ -\sinh(Q_2\eta/2)e^{-P_2\xi/2}], \quad \text{(III.7a)}$$

$$\psi_a=A_a[\cosh(Q_1\eta/2)e^{-P_1\xi/2} \\ +\sinh(Q_2\eta/2)e^{-P_2\xi/2}].$$

In the limit as r_n goes to ∞, we have $A_b=A_a=\pi^{-\frac{1}{2}}$, and

$$\psi_b\rightarrow\pi^{-\frac{1}{2}}e^{-r_b}, \quad \psi_a\rightarrow\pi^{-\frac{1}{2}}e^{-r_a}. \quad \text{(III.7b)}$$

Although these two states are not degenerate, in the limit of large internuclear separation, these eigenvalues E_1 and E_2 are sufficiently close to suggest that in a first approximation we proceed as with H_2^+ and diagonalize the appropriate 2×2 submatrix. The matrix elements are now:

$$\begin{aligned}
H_{11}&=\{\psi_b|\tfrac{1}{2}\epsilon\mathcal{E}r_n\cos\theta_n[\eta_1\xi_1-(M_a-M_b)/(M_a+M_b)]|\psi_b\}+E_1\\
&=\tfrac{1}{2}\epsilon\mathcal{E}r_n\cos\theta_n\{\tfrac{1}{2}A_b{}^2r_n{}^3[D_3E_{112}-D_1E_{312}]-(M_a-M_b)/(M_a+M_b)\}+E_1;\\
H_{22}&=\{\psi_a|\tfrac{1}{2}\epsilon\mathcal{E}r_n\cos\theta_n[\eta_1\xi_1-(M_a-M_b)/(M_a+M_b)]|\psi_a\}+E_2\\
&=\tfrac{1}{2}\epsilon\mathcal{E}r_n\cos\theta_n\{\tfrac{1}{2}A_a{}^2r_n{}^3[D_1E_{312}-D_3E_{112}]-(M_a-M_b)/(M_a+M_b)\}+E_2;\\
H_{12}&=H_{21}=(\psi_a|\tfrac{1}{2}\epsilon\mathcal{E}r_n\cos\theta_n[\eta_1\xi_1-(M_a-M_b)/(M_a+M_b)]|\psi_b)=0.
\end{aligned}\qquad\text{(III.8b)}$$

In the limit of large r_n, H_{11} and H_{22} reduce to

$$H_{11}\rightarrow-\tfrac{1}{3}(\tfrac{1}{2}\epsilon\mathcal{E}r_n)\cos\theta_n+E_1,$$

and

$$H_{22}\rightarrow+\tfrac{2}{3}(\tfrac{1}{2}\epsilon\mathcal{E}r_n)\cos\theta_n+E_2.$$

If we combine Eq. (III.8b) with the term

$$-e\mathcal{E}[(aM_b-bM_a)/(M_a+M_b)]z_n$$

which occurs explicitly in the nuclear Eq. (II.4), the asymptotic potentials for the nuclear motion are given by

$$E_b=-\tfrac{2}{3}\epsilon\mathcal{E}r_n\cos\theta_n+E_1,$$

and

$$E_a=+\tfrac{1}{3}\epsilon\mathcal{E}r_n\cos\theta_n+E_2.$$

These potentials are illustrated in Fig. 6. It is clear that, in the "classical" limit, the HD⁺ ion is more susceptible to dissociation than is H_2^+. One can readily show that, for the HT⁺ ion, the coefficients in the asymptotic nuclear potential are $-\frac{3}{4}$ and $+\frac{1}{4}$, respectively.

2. *Dissociation of HD*

The electronic wave function for the ground state of this two-electron system is taken to be

$$\psi_g=\mathfrak{A}\psi_a(1)\alpha(1)\psi_b(2)\beta(2).$$

The pertinent matrix element is written

$$\begin{aligned}H_{11}=(\psi_g|\tfrac{1}{2}\epsilon\mathcal{E}r_n\cos\theta_n\\
\times[\xi_1\eta_1+\xi_2\eta_2-2(M_a-M_b)/(M_a+M_b)]|\psi_g)+E_1.\end{aligned}$$

According to Eq. (III.9b), this reduces to

$$\begin{aligned}H_{11}=(\psi_a|\tfrac{1}{2}\epsilon\mathcal{E}r_n\cos\theta_n\xi_1\eta_1|\psi_a)\\
+(\psi_b|\tfrac{1}{3}\epsilon\mathcal{E}r_n\cos\theta_n\eta_1\xi_1|\psi_b)+\tfrac{1}{3}\epsilon\mathcal{E}r_n\cos\theta_n+E_1.\end{aligned}$$

If we use the results obtained for HD⁺, the first two terms cancel. Combining H_{11} with the explicit term $-\frac{1}{3}e\mathcal{E}Z_n$ appearing in the nuclear equation we have

$$H_{11}=E_1.$$

The nuclear potential is as illustrated in Fig. 2.

3. *Dissociation of LiH⁺*

The ground state of the LiH molecule has a large equilibrium separation and a relatively shallow potential minimum. No data exist on the properties of LiH⁺ ions, but we can suspect that these ions also will be loosely bound structures and hence relatively susceptible to dissociation.

The correlation diagram given by Herzberg indicates that the ground state of LiH⁺ consists of two occupied ψ_b orbitals and one ψ_a orbital.[21] In the limit of large r_n, LiH⁺ → Li⁺+H. Our ground-state wave function is

$$\psi_g=\mathfrak{A}\psi_b(1)\alpha(1)\psi_b(2)\beta(2)\psi_a(3)\alpha(3).$$

The matrix element becomes

$$\begin{aligned}H_{11}=\tfrac{1}{2}\epsilon\mathcal{E}r_n\cos\theta_n\\
\times\{2(\psi_b|\xi_1\eta_1|\psi_b)+(\psi_a|\xi_1\eta_1|\psi_a)+9/4\}+E_1;\\
H_{11}\rightarrow\tfrac{5}{8}\epsilon\mathcal{E}r_n\cos\theta_n+E_1.\end{aligned}$$

Combined with the term $-\frac{1}{2}e\mathcal{E}Z_n$ in the nuclear equation, the asymptotic nuclear potential becomes

$$E_g=\tfrac{1}{8}e\mathcal{E}r_n\cos\theta_n+E_1.$$

4. *Dissociation of LiH⁺⁺*

It is not known whether this ion possesses a stable ground state; however, a comparison of the asymptotic potential of this case with that of LiH⁺ illustrates the sensitive dependence of the problem on the charge states of the ion and its dissociation products. The LiH⁺⁺

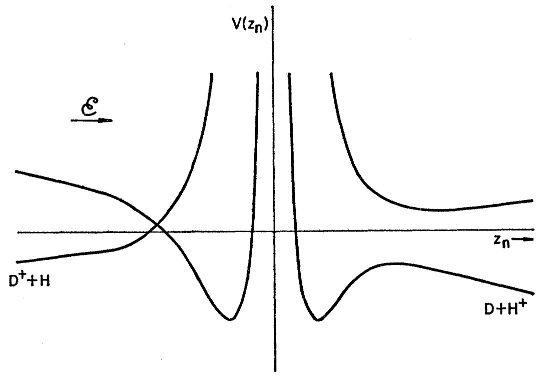

FIG. 6. The nuclear potential for HD⁺ in the presence of an electric field. The asymptotic potential for the lower electronic state varies as $-\frac{2}{3}\mathcal{E}z_n$.

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[21] G. Herzberg, *Spectra of Diatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1950).

dissociates according to $\mathrm{LiH}^{++}\rightarrow\mathrm{Li}^{+}+\mathrm{H}^{+}$. The wave function is now

$$\psi_g=\mathcal{A}\psi_b(1)\alpha(1)\psi_b(2)\beta(2),$$

and the matrix element is

$$H_{11}=\tfrac{1}{2}\epsilon\mathcal{E}r_n\cos\theta_n\{2(\psi_b|\xi_1\eta_1|\psi_b)+\tfrac{3}{2}\}+E_1.$$

In the limit of large r_n, we have

$$H_{11}=-\tfrac{1}{4}\epsilon\mathcal{E}r_n\cos\theta_n+E_1.$$

Combining H_{11} with $-\frac{1}{2}e\mathcal{E}Z_n$ term in the nuclear equation, we have for the asymptotic potential

$$E_g=-\tfrac{3}{4}e\mathcal{E}r_n\cos\theta_n+E_1.$$

C. Classical Treatment of Dissociation

We conclude Sec. III with an elementary discussion of the classical dissociation of two bodies. Let eA and eB be the charges of two dissociation fragments of masses M_A and M_B, respectively. Let $f(r_A-r_B)$ be a function describing the equivalent of the molecular binding forces and van der Waals forces. In the limit of large r_A-r_B, choose f to be zero. The forces on the bodies A and B are

$$M_A\ddot{r}_A=f(r_A-r_B)+eA\mathcal{E}$$

and

$$M_B\ddot{r}_B=-f(r_A-r_B)+eB\mathcal{E}.$$

Multiplying the first equation by M_B and the second by M_A and subtracting the second from the first, we obtain the equation for the relative motion:

$$(M_AM_B)/(M_A+M_B)\ddot{r}_n=f(r_n)+e\mathcal{E}[(AM_B-BM_A)/(M_A+M_B)].$$

In the limit of large r_n, the relative potential is given by

$$V(r_n)=-e\mathcal{E}[(AM_B-BM_A)/(M_A+M_B)]r_n.$$

This relative potential is in agreement with the asymptotic potential found in the previous sections. It is quite interesting that the correct classical asymptotic potential is obtained in the quantum-mechanical problem through contributions from both the electronic equation and the nuclear equation. The parameter $(AM_B-BM_A)/(M_A+M_B)$ provides a useful criterion for estimating the stability of various ions.

IV. DISSOCIATION BY A MAGNETIC FIELD

In this section we shall consider the equations of motion of an $\mathrm{H}_2{}^+$ ion moving in a uniform magnetic field. Our purpose is to examine to what extent the dissociation of the ion by the Lorentz force is equivalent to dissociation by an electrostatic field.

Let H be the intensity of the magnetic field which is taken in the z direction. The vector potential for this field is in the ϕ direction, $A_\phi=(H/2)\rho$, where $\rho=(x^2+y^2)^{\frac{1}{2}}$. The Hamiltonian for the system is given by

$$\left[\frac{1}{2M}\left(\mathbf{p}_a-\frac{e}{c}\mathbf{A}_a\right)^2+\frac{1}{2M}\left(\mathbf{p}_b-\frac{e}{c}\mathbf{A}_b\right)^2+\frac{1}{2m}\left(\mathbf{p}_e+\frac{e}{c}\mathbf{A}_e\right)^2+V_1\right]\psi=-(\hbar/i)\frac{\partial}{\partial t}\psi.$$

Introducing the transformation which led from Eq. (II.1) to Eq. (II.2) and writing H_0 for the Hamiltonian when $\mathbf{A}=0$, we have

$$\left[H_0-\frac{e\hbar}{iMc}(\mathbf{A}_a\cdot\boldsymbol{\nabla}_a+\mathbf{A}_b\cdot\boldsymbol{\nabla}_b)+\frac{e\hbar}{imc}\mathbf{A}_e\cdot\boldsymbol{\nabla}_e+\frac{e^2}{2Mc^2}(A_a{}^2+A_b{}^2)+\frac{e^2}{2mc^2}A_e{}^2\right]\psi=W\psi.$$

Neglecting quantities of order m/M compared with unity, using $A_x=-(H/2)y$ and $A_y=(H/2)x$, the sum of the second and third terms can be shown to reduce to

$$\mathrm{II}+\mathrm{III}=\frac{eH\hbar}{2Mic}\left[\frac{1}{2}\frac{\partial}{\partial\phi_c}+\frac{\partial}{\partial\phi_n}+\frac{1}{2}\left(x_1\frac{\partial}{\partial y_c}-y_1\frac{\partial}{\partial x_c}\right)\right]+\frac{eH\hbar}{2mic}\left[\frac{\partial}{\partial\phi_1}+\left(x_c\frac{\partial}{\partial y_1}-y_c\frac{\partial}{\partial x_1}\right)\right].$$

Considering the A^2 terms, we note that we have $r_n\ll r_c$ and $r_1\ll r_c$. If we write $\rho_a\simeq\rho_c$, $\rho_b\simeq\rho_c$, and $\rho_e\simeq\rho_c$, the A^2 terms reduce to

$$(e^2/2Mc^2)(A_a{}^2+A_b{}^2)+(e^2/2mc^2)A_e{}^2\simeq(e^2H^2/8mc^2)\rho_c{}^2.$$

The second term in II+III is the Zeeman term in the nuclear coordinates and is equal to $(eH/2Mc)\times\hbar[J(J+1)]^{\frac{1}{2}}$, where J is the rotational quantum number. The fourth term is the Zeeman term in the electronic coordinates. These Zeeman terms are usually small compared with the separation of the vibrational levels, and for the purposes of this problem can be neglected. For the fifth term, we use $(\hbar/im)(\nabla_1)=v_1$, where v_1 is the expectation value of the internal electron velocity. This term can be combined with the first term and is negligibly small when the center-of-mass velocity is large compared with v_1.

The third term is the term of interest. If we write $(\hbar/2iM)(\nabla_c)=(v_c)$, and take the center-of-mass motion to be a classical circular trajectory, this term becomes

$$\frac{eH\hbar}{2Mci}\frac{1}{2}\left(x_1\frac{\partial}{\partial y_c}-y_1\frac{\partial}{\partial x_c}\right)=\frac{eHv_c}{2c}(x_1\sin\omega t-y_1\cos\omega t),$$

where $\omega=eH/2Mc$.

Consider next a transformation of the electronic and nuclear coordinates into a coordinate system rotating with angular velocity ω; the third term becomes

$-(eH/2c)v_c y'_1$. If we set $\mathcal{E}=v_c H/c$, the electronic and nuclear equations have the same form as Eq. (III.1) and Eq. (III.5), respectively.

V. CONCLUSIONS

The primary mode of electric dissociation of molecular ions is predissociation. Neutral molecules and homonuclear molecular ions with an even charge state dissociate via electron stripping. The asymptotic nuclear potential for homonuclear ions with an odd charge state varies as $-\frac{1}{2}e\mathcal{E}|z_n|$. For heteronuclear molecular ions, the asymptotic dependence of the nuclear potential and hence the susceptibility to electric dissociation is a function of the masses and charge states of the dissociation products.

The transition rate for dissociation is a sensitive function of the initial vibrational state of the ion. The necessary fields for dissociating the H_2^+ ion range from 10^5 v/cm for the uppermost vibrational state to 2×10^8 v/cm for the ground state. The HD^+ and HT^+ ions are more susceptible to dissociation than is H_2^+.

The acceleration of H_2^+ ions in cyclotrons and other circular accelerators can be extended into the Bev range. Since the lower vibrational states of the H_2^+ ion are generally more densely populated than the upper states, no significant beam losses from predissociation will occur in conventional circular accelerators at energies below 1 Bev.

In the application of this work to the injection problem for controlled-fusion experiments, effective electric fields of the order of 10^6 v/cm can be considered. For those molecular ions in which predissociation is the primary dissociation mode, several of the uppermost vibrational states are susceptible to dissociation for fields within this range. For an electric field of 10^6 v/cm, the required time for inducing transitions between the upper vibrational states is of order 10^{-3} sec; these induced transitions will not interfere with the more rapid predissociation. The recent experiment of Anderson *et al.*[22] has shown that most of the vibrational states of the H_2^+ ion remain populated when such ions are accelerated in Van de Graaf machines. The practical utilization of the injection method considered here will require further demonstration that the uppermost vibrational states can be populated.

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APPENDIX

Various integrals encountered in Sec. III are defined here. These integrals are readily evaluated with standard integral tables.

$$E_{mn}=\int_1^\infty \xi^m e^{P_n\xi}d\xi;$$

$$E_{m12}=\int_1^\infty \xi^m e^{-\frac{1}{2}(P_1+P_2)\xi}d\xi;$$

$$B_m=\int_{-1}^{+1} \eta^m \sinh(Q\eta/2)\cosh(Q\eta/2)d\eta;$$

$$C_m=\int_{-1}^{+1} \eta^m \cosh^2(Q\eta/2)d\eta;$$

$$D_m=\int_{-1}^{+1} \eta^m \sinh(Q_2\eta/2)\cosh(Q_1\eta/2)d\eta;$$

$$F_m=\int_{-1}^{+1} \eta^m \sinh^2(Q\eta/2)d\eta.$$

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[22] S. L. Anderson, K. Gjotterud, T. Holtebekk, and O. Lonsjo, Nuclear Phys. 7, 384 (1958).