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DISSOCIATION OF MOLECULAR IONS BY ELECTRIC FIELDS

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ABSTRACT

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  $2 \times 10^8$  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 dissociation than is  $H_2^+$ . The extent to which the dissociation by an electrostatic field and by the Lorentz force,  $e\vec{v} \times \vec{B}$ , 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.

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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).<sup>1</sup> These calculations have been extended to various excited states of the hydrogen atom by Lanczos.<sup>2</sup>

The nature of the process is such that the presence of the external field brings about a change in the potential experienced by the atomic electron in such a way that the bound electron sees a barrier of finite width through which it can tunnel its way to freedom. A general property of such tunneling processes is that the transition rate depends exponentially on the height of the barrier. In the atomic problem, this barrier height is at least approximately defined by the energy required to excite an electron into the continuum.

Consequently one would expect that the field magnitudes calculated by Oppenheimer to be necessary for an observable dissociation

rate might be markedly reduced in a system whose pertinent binding energy is appreciably less than that of the hydrogen atom.

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 are 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 then that an ion for which the uppermost vibrational states of a particular electronic state are occupied would provide an example of a system that would dissociate at a reasonable rate in the presence of an appreciably smaller field than is required for atomic dissociation. This mode of dissociation, in which the molecular system divides into two atomic systems -- a form of predissociation -- appears to be the principal mode of dissociation for most molecular ions.

Apart from its general physical interest, this mechanism has application to particle accelerators and to the injection problem for controlled-fusion devices. The inspiration for this work originated with some remarks by members of the Princeton accelerator group who, in considering the possibility of accelerating  $H^-$  ions in an accelerator and then trapping these ions in a storage ring by changing their charge state to  $H^+$ , recognized that the  $H^-$  ion is quite susceptible to dissociation into an H atom and a free electron through the action of the Lorentz force,  $e\vec{v} \times \vec{B}$ .<sup>3,4</sup> This "Lorentz dissociation" of  $H^-$  may have



been observed by Lofgren in the 184-in. cyclotron.<sup>5,6</sup>

It was recognized that such a mechanism for changing the charge state of an atomic system might find application as an injection mechanism for fusion devices employing large magnetic fields. Such change-of-charge-state mechanisms employing atomic and molecular systems as a means for trapping energetic particles inside a magnetic field region had previously been proposed utilizing conventional ionization processes.<sup>7,8</sup>

The basic requirement of such injection methods is simply that the absolute value of the ratio of charge to mass of the atomic system must increase during the respective ionization process. The stripping of electrons from negative ions by the Lorentz force is therefore not of interest. The stripping of electrons from the ground state of neutral atoms is limited by the requirement of intense fields; the Li atom with a binding energy of 5.36 electron volts (ev) would appear to require electric fields in excess of  $10^7$  v/cm to achieve a useful dissociation rate. (In later sections it will be shown that the neutral molecule is appreciably more susceptible to dissociation than the corresponding atom.)

These considerations have prompted a study of the dissociation of the simplest molecular structure, the hydrogen molecular ion. 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.<sup>9</sup>

The extent to which these two problems are equivalent is discussed in Appendix D; in this appendix it is shown that provided one ignores the Zeeman terms, which are negligibly small compared to the separations of

the vibrational levels, the dissociation by a magnetic field reduces to the problem of the dissociation by an electric field. A preliminary report of this work on  $H_2^+$  has already been given.<sup>10</sup>

It is conventional in many cyclotron establishments to accelerate  $H_2^+$  as a source of protons. As cyclotron energies are increased, it is of interest to inquire into the stability of successive vibrational states. The curves included in this work should be useful in providing a basis for estimating these successive stabilities. It is interesting to note that on the basis of an instantaneous Lorentz transformation into a system moving with the ion, which yields  $\vec{C} = \gamma \vec{v} \times \vec{B}$ , one concludes that an ion in its ground vibrational state is stable for acceleration up to some 60 Bev in a 20 kilogauss field.

At an early point it was recognized that an accurate treatment of the dissociation would require a knowledge of the vibrational eigenfunctions and eigenvalues belonging to the ground electronic state of  $H_2^+$ . These calculations have been carried out in collaboration with Dr. Stanley Cohen and Dr. Robert J. Riddell, Jr., utilizing potential functions calculated in connection with the mesonic-molecule work.<sup>11</sup> These calculations are reported elsewhere.<sup>12</sup>

Following the publication of the preliminary report mentioned above, an additional bound vibrational state lying between what had been thought to be the uppermost state and the dissociation limit was discovered. The original paper together with the later work on  $H_2^+$  is included in this paper; a report on this later work has already been given.<sup>13</sup>

The extension of this problem to the many-electron system and to heteronuclear molecules has been facilitated by the recent work of Dalgarno and McCarroll,<sup>14</sup> and that of Cohen, Judd, and Riddell.<sup>15</sup>

In Section II the equations for a general many-electron diatomic molecule moving in the presence of electrostatic field are developed. Included in Section II is a discussion of the electromagnetic transitions between the vibrational states of the general diatomic molecule.

In Section III the general equations of the previous section are applied to several particular molecular ions. The  $H_2^+$  system is treated in considerable detail, followed by a general discussion of the many-electron homonuclear system in successive charge states. The treatment on heteronuclear molecules is applied to the  $HD^+$ ,  $HD$ ,  $LiH^+$ , and  $LiH^{++}$  systems. Finally, an elementary classical analogy to molecular predissociation is derived for comparison with the quantum-mechanical results.

## II. THE GENERAL EQUATIONS

### A. Separation of the Motions

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

Consider an  $n$ -electron diatomic molecule with nuclei of masses  $M_a$  and  $M_b$  and charges  $e_a$  and  $e_b$  in the presence of an electrostatic field. Let  $\vec{r}_a$ ,  $\vec{r}_b$ , and  $\vec{r}_{ei}$  represent the coordinates of the two nuclei and the  $i$ th electron, respectively, all measured with respect to the laboratory system. Take the direction of the  $z$  axis along the electric field. The

Schroedinger equation for this system is written

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

where

$$V_1 = \frac{a b e^2}{|\vec{r}_a - \vec{r}_b|} - \sum_{i=1}^n \left[ \frac{a e^2}{|\vec{r}_a - \vec{r}_{ei}|} + \frac{b e^2}{|\vec{r}_b - \vec{r}_{ei}|} \right] + \frac{1}{2} \sum_{i=1}^n \sum_{j \neq i}^n \frac{e^2}{|\vec{r}_{ei} - \vec{r}_{ej}|} \quad (\text{II.1b})$$

and

$$V_2 = -e\mathcal{E} \left[ a z_a + b z_b - \sum_{i=1}^n z_{ei} \right] \quad (\text{II.1c})$$

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,  $\vec{r}_c$ , a relative nuclear coordinate,  $\vec{r}_n$ , and n additional coordinates,  $\vec{r}_i$ , measuring the distance of the ith electron from the center of mass of the two nuclei. The transformation is written:

$$\begin{aligned} \vec{r}_c &= \rho_a \vec{r}_a + \rho_b \vec{r}_b + \rho \sum_{i=1}^n \vec{r}_{ei} \\ \vec{r}_n &= \vec{r}_a - \vec{r}_b \\ \vec{r}_i &= \vec{r}_{ei} - f_a \vec{r}_a - f_b \vec{r}_b , \end{aligned} \quad (\text{II.2})$$

where:

$$\rho_a = \frac{M_a}{M_a + M_b + nm}$$

$$\rho_b = \frac{M_b}{M_a + M_b + nm}$$

$$\rho = \frac{m}{M_a + M_b + nm}$$

$$f_a = \frac{M_a}{M_a + M_b}$$

$$f_b = \frac{M_b}{M_a + M_b}$$

When this transformation is introduced into Eq. (II.1), the Schroedinger equation in these new coordinates becomes

$$\begin{aligned}
 -\frac{\hbar^2}{2} \left\{ \frac{1}{M_a + M_b + nm} \nabla_c^2 + \frac{M_a + M_b}{M_a M_b} \nabla_n^2 + \frac{1}{M_a + M_b} \sum_i^n \sum_{j \neq i}^n \nabla_i \cdot \nabla_j \right. \\
 \left. + \frac{M_a + M_b + m}{m(M_a + M_b)} \sum_{i=1}^n \nabla_i^2 \right\} \psi \\
 + \left\{ V_1 + V_2 \right\} \psi = E\psi,
 \end{aligned} \tag{II.3a}$$

with

$$V_1 = \frac{ab e^2}{|\vec{r}_n|} - \sum_{i=1}^n \frac{ae^2}{|\vec{r}_i - f_2 \vec{r}_n|} + \frac{be^2}{|\vec{r}_i + f_1 \vec{r}_n|} + \frac{1}{2} \sum_{i=1}^n \sum_{j \neq i}^n \frac{e^2}{|\vec{r}_i - \vec{r}_j|} .$$

(II.3b)

In Appendix A it is shown that

$$\begin{aligned}
 V_2 = -e\mathcal{E} \left[ a + b - n \right] z_c - e\mathcal{E} \left[ \frac{a M_b - b M_a}{M_a + M_b} \right] z_n \\
 + e\mathcal{E} \left[ 1 + \frac{(a + b - n)m}{M_a + M_b + nm} \right] \sum_{i=1}^n z_i .
 \end{aligned} \tag{II.3c}$$

The center-of-mass motion can now be separated from the equation for the internal motion by writing

$$\psi(\vec{r}_c, \vec{r}_n, \vec{r}_i) = \pi(\vec{r}_c) \psi(\vec{r}_n, \vec{r}_i)$$

and

$$E = E_c + W .$$

The equation for the center-of-mass motion becomes

$$\left\{ -\frac{\hbar^2}{2} \left[ M_a + M_b + nm \right]^{-1} \nabla_c^2 - e\mathcal{E} \left[ a + b - n \right] z_c \right\} \pi = E_c \pi .$$

This equation describes the motion of a particle of mass  $M_a + M_b + nm$  and charge  $e(a + b - n)$  moving in an electrostatic field.

The equation for the internal motions is written

$$\begin{aligned}
 & -\frac{\hbar^2}{2} \left\{ \frac{1}{M_n} \nabla_n^2 + \frac{1}{M_a + M_b} \sum_i^n \sum_{j \neq i} \vec{\nabla}_i \cdot \vec{\nabla}_j + \frac{1}{m_e} \sum_i^n \nabla_i^2 \right\} \psi \\
 & + \left\{ V_1 - e\mathcal{E} \left[ \frac{aM_b - bM_a}{M_a + M_b} \right] z_n + e\mathcal{E} \left[ 1 + \frac{(a+b-n)m}{M_a + M_b + nm} \right] \sum_i^n z_i \right\} \psi = W\psi,
 \end{aligned} \tag{II.4}$$

with

$$M_n = \frac{M_a M_b}{M_a + M_b}$$

and

$$m_e = \frac{m(M_a + M_b)}{M_a + M_b + m}$$

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

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

Inserting this expansion into Eq. (II.4), multiplying by  $\psi_\lambda^*$ , and integrating over all electronic coordinates, we have

$$\begin{aligned}
 & -\frac{\hbar^2}{2M_n} \nabla_n^2 \chi_\lambda + \left[ \frac{abe^2}{r_n} - e\mathcal{E} \left( \frac{aM_b - bM_a}{M_a + M_b} \right) z_n + E_\lambda(r_n) - w \right] \chi_\lambda + \epsilon_{\lambda K} \\
 & + \sum_K \chi_K \int \psi_\lambda^* \left\{ -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 - \sum_{i=1}^n \left[ \frac{ae^2}{|\vec{r}_i - f_2 \vec{r}_n|} + \frac{be^2}{|\vec{r}_i + f_1 \vec{r}_n|} \right] \right. \\
 & + \frac{1}{2} \sum_{i=1}^n \sum_{j \neq i}^n \frac{e^2}{|\vec{r}_j - \vec{r}_i|} \\
 & \left. + e\mathcal{E} \left[ 1 + \frac{(a+b-n)m}{M_a + M_b + nm} \right] \sum_{i=1}^n z_i - E_\lambda(r_n) \right\} \psi_K d^3r_1 \dots d^3r_n, \tag{II.5}
 \end{aligned}$$

where

$$\begin{aligned} \epsilon_{\lambda K} = & \frac{1}{M_n} \left[ \sum_K x_K \int \psi_\lambda^* \nabla_n^2 \psi_K d^3r_1 \dots d^3r_n + 2 \sum \int \psi_\lambda^* \nabla_n \cdot \nabla_n \psi_K d^3r_1 \dots d^3r_n \right] \\ & + \frac{1}{M_a + M_b} \sum_K x_K \int \psi_\lambda^* \sum_i \sum_{j \neq i} \nabla_i \cdot \nabla_j \psi_K d^3r_1 \dots d^3r_n . \end{aligned}$$

The electronic functions,  $\psi_K$ , are defined by setting the bracketed quantity in the integrand of Eq. (II.5) 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  $\epsilon_{\lambda K}$  series to zero. The various vibrational states belonging to a particular electronic state,  $E_\lambda$ , are then determined by the equation

$$-\frac{\hbar^2}{2M_n} \nabla_n^2 x_\lambda + \left[ \frac{abe^2}{r_n} - e\zeta \left( \frac{aM_b - bM_a}{M_a + M_b} \right) Z_n + E_\lambda(r_n) - W \right] x_\lambda = 0. \quad (\text{II.6})$$

For homonuclear molecules, the  $\epsilon_{\lambda K}$  series is a simple correction to the nuclear potential, the leading term in this series contributing a quantity of order  $m/M_n$ .<sup>15</sup> 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 potential, the leading terms in  $\epsilon_{\lambda K}$  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.<sup>15</sup> 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 the nature of these vibrational transitions, particularly with respect to quadrupole transitions in homonuclear molecules.

In Appendix B, the spontaneous-transition rate for dipole transitions is shown to be

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

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  $\chi_{10} \approx 0.22$  ev and  $\bar{r}_n \approx 2a_0$ . The lifetime of this first excited state is approximately 200 microseconds ( $\mu\text{sec}$ ). 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

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



These quadrupole lifetimes are approximately a factor of  $\left(\frac{2}{a} \frac{\lambda}{r_n}\right)^2$  longer than are the dipole lifetimes.

(2) Induced Transitions

Switching on 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 Appendix B, it is shown that the induced transition rate is given approximately by

$$T_1 = \frac{4}{3} \frac{e^4}{c^3} \frac{v_{kj} \epsilon^2}{h^3} \left| \left( \psi_2 x_k \left| r_1 r_n \cos \theta_n \right| \psi_2 x_j \right) \right|^2$$

These transitions have been discussed previously by Condon.<sup>16</sup>

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 previous 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.5) 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 hydrogen molecular ion. We begin the discussion by considering the electronic equation for this one-electron system:

$$\left\{ \frac{-\hbar^2}{2m_e} \nabla_1^2 - \left[ \frac{e^2}{|\vec{r}_1 - \frac{1}{2} \vec{r}_n|} + \frac{e^2}{|\vec{r}_2 + \frac{1}{2} \vec{r}_n|} - \xi \mathcal{E} z_1 \right] \right\} \psi_K = E_K(r_n) \psi_K, \quad (\text{III.1})$$

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

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  $\xi \mathcal{E} z_1$  is to perturb the electronic eigenvalues. This perturbation in turn leads to a disruption of the nuclear motion. Before considering this effect, we digress to consider some properties of the unperturbed ion.

The unperturbed hydrogen molecular ion has been discussed fairly extensively in the literature, and we have available several choices

for the electronic functions,  $\psi_K$ . The simplest function is the linear combination of atomic orbitals (L.C.A.O.) approximation in which the electronic state is taken as a linear combination of hydrogenic wave functions centered about the two protons. For the ground state and first excited state these are explicitly written:

$$\begin{aligned}\psi_1 &= [2(1 + T)]^{-1/2} \left\{ \phi_a(1s) + \phi_b(1s) \right\} \\ \psi_2 &= [2(1 - T)]^{-1/2} \left\{ \phi_a(1s) - \phi_b(1s) \right\},\end{aligned}\quad (\text{III.2a})$$

where

$$\begin{aligned}\phi_a(1s) &= \frac{1}{\sqrt{\pi}} e^{-|\vec{r}_1 - \frac{1}{2}\vec{r}_n|/a_0}, \\ \phi_b(1s) &= \frac{1}{\sqrt{\pi}} e^{-|\vec{r}_1 + \frac{1}{2}\vec{r}_n|/a_0},\end{aligned}$$

and

$$T = \int \phi_a \phi_b d^3r_1.$$

The molecular designation for these two states are  $\sum_g^{2+}$  and  $\sum_u^{2+}$ ,

respectively. Although these functions provide a good approximation for large internuclear separation, they are known to be poor in the limit of small separation. However, in a discussion of dissociation we are interested primarily in effects at large internuclear separation, and these functions are useful.

The Eq. (III.1) for  $\xi = 0$  is separable in confocal elliptic coordinates  $\xi, \eta, \Phi$ . These coordinates are defined by

$$\xi = \frac{|\vec{r}_{el} - \vec{r}_a| + |\vec{r}_{el} - \vec{r}_b|}{|\vec{r}_a - \vec{r}_b|} = \frac{|\vec{r}_1 - \frac{1}{2}\vec{r}_n| + |\vec{r}_1 + \frac{1}{2}\vec{r}_n|}{|\vec{r}_n|} = \frac{r_a + r_b}{r_n}$$

and

$$\eta = \frac{|\vec{r}_{el} - \vec{r}_b| - |\vec{r}_{el} - \vec{r}_a|}{|\vec{r}_a - \vec{r}_b|} = \frac{|\vec{r}_1 + \frac{1}{2}\vec{r}_n| - |\vec{r}_1 - \frac{1}{2}\vec{r}_n|}{|\vec{r}_n|} = \frac{r_b - r_a}{r_n},$$

where  $r_a$  and  $r_b$  measure the distances of the electron from proton a and proton b, respectively. These scalar functions are not to be confused with the vector functions defined previously in connection with Eq. (II.1).

If  $x''$ ,  $y''$ , and  $z''$  are the coordinates oriented with respect to the internuclear axis and with origin at the midpoint of a and b, these coordinates are related to the  $\xi$ ,  $\eta$ ,  $\phi$  coordinates by

$$\begin{aligned} x'' &= \frac{r_n}{2} (\xi^2 - 1)^{1/2} (1 - \eta^2)^{1/2} \cos \phi, \\ y'' &= \frac{r_n}{2} (\xi^2 - 1)^{1/2} (1 - \eta^2)^{1/2} \sin \phi, \\ \text{and} \\ z'' &= \frac{r_n}{2} \xi \eta. \end{aligned} \quad (\text{III.3})$$

The volume element is

$$d\tau = \frac{r_n^3}{8} (\xi^2 - \eta^2) d\xi d\eta d\phi,$$

and the range of the variables is given by  $1 \leq \xi < \infty$ ,  $-1 \leq \eta \leq 1$ , and  $0 \leq \phi \leq 2\pi$ .

Introducing these coordinates into Eq. (III.1), there result three separated equations -- one trivial, the other two requiring numerical integration for their general solution.<sup>17,18,19</sup> These integrations have also been carried out by Bates, Ledsham, and Stewart for several electronic states; the results are tabulated over a range  $0 \leq r_n/a_0 \leq 10$ .<sup>20</sup>

A third set of functions have been given by Cohen, Judd, and Riddell<sup>15</sup> using a variational calculation in confocal elliptic coordinates. Their variational functions are of the form

$$\begin{aligned} \psi_1 &= A_1 \cosh \frac{q_1(r_n)\eta r_n}{2} e^{-\frac{p_1(r_n)\xi r_n}{2}} \\ \text{and} \\ \psi_2 &= A_2(\xi) \sinh \frac{q_2(r_n)\eta r_n}{2} e^{-\frac{p_2(r_n)\xi r_n}{2}}. \end{aligned} \quad (\text{III.2b})$$

Here the variational parameters  $p(r_n)$  and  $q(r_n)$ , are tabulated for the interval  $0 \leq \frac{r_n}{a_0} \leq 20$ . The coefficients  $A_1$  and  $A_2$  are determined by the normalization conditions

$$\frac{\pi A_1^2}{4} r_n^3 \left[ E_2 C_0 - E_0 C_2 \right] = 1$$

and

$$\frac{\pi A_2^2}{4} r_n^3 \left[ E_2 B_0 - E_0 B_2 \right] = 1 .$$

The quantities  $E$ ,  $B$ , and  $C$  are defined and evaluated in Appendix C. In the limit of large internuclear separation, we have  $p = q = 1$ , and  $A_1 = A_2 = (2/\pi)^{1/2}$ .

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  $\psi_1$  and  $\psi_2$  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  $\psi_1$  and  $\psi_2$  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. The matrix to be diagonalized is then

$$\begin{pmatrix} H_{11} & H_{12} \\ H_{21} & H_{22} \end{pmatrix} . \quad (\text{III.4})$$

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  $\lambda$  and  $\mu$ , we have

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

The functions (III.2) are independent of  $\phi$ , and upon examining the transformation (III.3) we see that the terms in  $x''$  and  $y''$  vanish under the  $\phi$  integration. Noting that  $\cos \mu \cos \lambda = \cos \theta_n$ , where  $\theta_n$  is the angle between the internuclear axis and the electric-field direction, the relevant perturbation is then

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

The matrix elements are evaluated by using the functions given in Eqs. (III.2a) and (III.2b). In the former case we have

$$H_{11} = \int \psi_{E_1}^* \left[ H_0 + \epsilon \mathcal{E} z_1'' \right] \psi_1 d^3 \vec{r}_1 = E_1(r_n)$$

and

$$H_{22} = \int \psi_{E_2}^* \left[ H_0 + \epsilon \mathcal{E} z_1'' \right] \psi_2 d^3 \vec{r}_1 = E_2(r_n) .$$

Since the term in  $z_1''$  in the integrands is an odd function, the diagonal terms are unperturbed. For the off-diagonal term

$$\begin{aligned} H_{21} = H_{12} &= \int \psi_{E_2}^* \left[ H_0 + \epsilon \mathcal{E} z_1'' \right] \psi_1 d^3 \vec{r}_1 \\ &= + \frac{\epsilon \mathcal{E}}{2(1 - T^2)} (\varphi_a^2 - \varphi_b^2) z_1'' d^3 \vec{r}_1 \quad \text{(III.5a)} \\ &= + \frac{\epsilon \mathcal{E}}{2(1 - T^2)} r_n \cos \theta_n , \end{aligned}$$

where  $\theta_n$  is the angle between the electric-field direction (z axis) and the line joining the two nuclei.

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

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

The matrix elements are given by

$$H_{11} = E_1, \quad (\text{III.5b})$$

$$H_{22} = E_2, \quad (\text{III.5c})$$

and

$$H_{12} = H_{21} = \frac{\pi}{8} \epsilon \xi \cos \theta_n A_1 A_2 r_n^4 \left[ E_3 D_1 - E_1 D_3 \right]. \quad (\text{III.5d})$$

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

$$\frac{\pi}{8} \epsilon \xi \cos \theta_n A_1^2 r_n^4 \left[ E_{31} C_1 - E_{11} C_3 \right]$$

and

$$\frac{\pi}{8} \epsilon \xi \cos \theta_n A_2^2 r_n^4 \left[ E_{32} F_1 - E_{12} F_3 \right],$$

respectively, are each identically zero, in agreement with the result

using the LCAO functions. In the limit as  $r_n \rightarrow \infty$ , we have

$$H_{12} \rightarrow \frac{1}{2} \epsilon \xi r_n \cos \theta_n.$$

An integral similar to that occurring in the  $H_{12}$  term occurs in the theory of photodissociation. This integral has been evaluated numerically by Bates<sup>21</sup> using the exact numerical wave functions and a comparison of this result with the value given by the LCAO approximation. The agreement is excellent for large internuclear separations, significant deviations exist only for  $\frac{r_n}{a_0} < 2$ .

With these matrix elements, diagonalization of Eq. (III.4) yields two new electronic states,  $\psi_g$  and  $\psi_u$ , whose eigenvalues are, respectively,

$$E_g = \frac{E_1 + E_2}{2} - \frac{1}{2} (E_2 - E_1) \left[ 1 + \frac{\epsilon^2 \xi^2 r_n^2 \cos^2 \theta_n}{(1 - T^2)(E_2 - E_1)^2} \right]^{\frac{1}{2}}$$

and

$$E_u = \frac{E_1 + E_2}{2} + \frac{1}{2} (E_2 - E_1) \left[ 1 + \frac{\epsilon^2 \xi^2 r_n^2 \cos^2 \theta_n}{(1 - T^2)(E_2 - E_1)^2} \right]^{\frac{1}{2}}. \quad (\text{III.6a})$$

For small values of  $r_n$  these reduce to

$$E_g = E_1 - \frac{1}{4} \frac{\epsilon^2 \mathcal{E}^2 r_n^2 \cos^2 \theta_n}{(1 - T^2)(E_2 - E_1)}$$

and

$$E_u = E_2 + \frac{1}{4} \frac{\epsilon^2 \mathcal{E}^2 r_n^2 \cos^2 \theta_n}{(1 - T^2)(E_2 - E_1)}, \quad (\text{III.6b})$$

and for large values of  $r_n$ , to

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

and

$$E_u = E_2 + \frac{\epsilon \mathcal{E} r_n |\cos \theta_n|}{2}. \quad (\text{III.6c})$$

Equations (III.6) indicate that the electronic eigenvalue, which in the unperturbed case was independent of the orientation of the internuclear axis, now has a value that is dependent on the nuclear orientation and in addition is a function of the electric-field value. We have seen in Eq. (II.5) how the electronic eigenvalue appears as part of the potential function for the nuclear motion. The nuclear potential which was spherically symmetric in the unperturbed case becomes axially symmetric in the perturbed case, with the axis of symmetry oriented along the field direction. The nuclear potential for the lowest electronic state now acquires a double-ended spout, the two spouts oriented along the field direction. The effect of the perturbation goes to zero in a direction at right angles to the nuclear axis in this approximation. The potential function for the upper electronic state also acquires a double-ended spout, but for this state the two spouts are oriented at right angles to the electric-field direction.

In Fig. 2 is shown the unperturbed nuclear potential for the two lowest electronic states. Conventionally these potentials are drawn



in a spherical-coordinate system, but for the purposes of this discussion a cylindrical-coordinate system is more appropriate. The vibrational states are indicated schematically by the light horizontal lines; for the  $H_2^+$  ion there are actually 19 bound vibrational 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 invariance of the Hamiltonian (II.4) 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  $H_2^+ \rightarrow H + p$ . 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

$$\psi_g = \left[ (E_g - E_2)^2 + H_{12}^2 \right]^{-1/2} \left\{ (E_g - E_2) \psi_1 + H_{12} \psi_2 \right\}$$

and

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

(III.7a)

Consider first the limit as  $r_n$  becomes large and the nuclear axis is aligned along the electric field, corresponding to proton lying

in the direction of the electric field with respect to proton b.

(since  $r_n \cos \theta_n = z_n = z_a - z_b$ ). In this limit we have  $E_g = E_2 = -|H_{12}|$ , and  $H_{12}/|H_{12}| = +1$ . Using Eq. (III.2a), we have

$$\psi_g \rightarrow \phi_b$$

and

$$\psi_u \rightarrow \phi_a \quad (III.7b)$$

Statement (III.6b) is 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. The dependence of the potential on the right-hand side of Fig. 3 is then understood.

If the internuclear axis is rotated 90 degrees to the field direction, the effect of the perturbation goes to zero. In this case we have

$$\psi_g \rightarrow \psi_1 \quad (III.7c)$$

$$\psi_u \rightarrow \psi_2,$$

and the electron has equal probability of being associated with either proton. Continue the rotation until the internuclear axis is oriented at 180 degrees with respect to its original direction; proton b now lies in the direction of the field with respect to proton a. For this case we have  $H_{12}/|H_{12}| = -1$ , and the electronic states become

$$\psi_g \rightarrow \phi_a \quad (III.7d)$$

and

$$\psi_u \rightarrow \phi_b$$

For the ground state, the electron is associated with proton a and proton b is free. Separating the nuclei corresponds to moving the charged proton b in the positive-electric-field direction, which lowers the potential. For the upper state, proton a is moved against the field and the potential is raised. This interpretation is consistent with the variation of the potential on the left-hand side of Fig. 3.

The higher-order effects which were neglected in diagonalizing the submatrix (III.3) can be estimated by using perturbation theory and taking as the basis functions the two solutions of Eq. (III.6a) together with all the unperturbed higher-state functions. In the limit as  $r_n$  goes to zero, the molecular ion degenerates into a  $\text{He}^+$  ion in its 1S state. The Stark shift for this state is

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

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

$$\Delta E = -\frac{9}{4} a_0^3 \mathcal{E}^2 . \quad (\text{III.6d})$$

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 can now consider in detail the nuclear dissociation. The equation for the nuclear motion is given by

$$\left\{ -\frac{\hbar^2}{2M_n} \nabla_n^2 + \frac{e^2}{r_n} + E_g(r_n, \theta_n, \mathcal{E}) - W_{lv} \right\} X_{lv} = 0 . \quad (\text{III.7a})$$

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

$$\left\{ -\frac{\hbar^2}{2M_n} \nabla_n^2 + E_1(r_n) - \frac{1}{2} \epsilon \mathcal{E} r_n |\cos \theta_n| - W_{1v} \right\} X_{1v} = 0. \quad (\text{III.7b})$$

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

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 use Oppenheimer's formula for the transition rate.<sup>1</sup> The method consists of solving for the motion of the ion in the asymptotic region given by Eq. (III.7b) and neglecting the binding effects of the molecular forces at small internuclear separation. The transition is then imagined to proceed from the bound discrete vibrational state of the ion to the unbound free-state solution, the perturbation inducing the transition being a function of  $\mathcal{E}$ . Specifically, the matrix element for the transition is written

$$(X_A | \Delta V | X_{1v}),$$

where

$$\Delta V = \frac{E_2 - E_1}{2} - \frac{1}{2} \left\{ (E_2 - E_1)^2 + 4 H_{12}^2 \right\}^{1/2}$$

$X_{1v}$  is bound vibrational state, and  $X_A$  is a solution of Eq. (III.7b).

For these calculations, it was found that the primary contributions to the matrix element come in the range where

$$\Delta V \approx -\frac{1}{2} \epsilon \mathcal{E} Z_n.$$

The solutions of Eq. (III.7b) in cylindrical coordinates  $\rho_n, z_n,$   
 $\phi_n$  for the classical and nonclassical regions and normalized to a  
 continuous spectra are, respectively,

$$\chi_{AC} = 2^{5/3} \sqrt{\frac{\pi}{3}} \frac{M_n}{\hbar} (3\alpha)^{-1/6} \gamma^{1/3} \left\{ J_{1/3}(\gamma) + J_{-1/3}(\gamma) \right\} J_{\sqrt{\lambda_3}} \left( \sqrt{\lambda_2} \rho_n \right) \\ \times e^{i \sqrt{\lambda_3} \phi_n}$$

and

$$\chi_{ANC} = - 2^{2/3} \frac{M_n}{\hbar} \sqrt{\pi} (3\alpha)^{-1/6} i^{2/3} \gamma^{1/3} H_{1/3}^{(2)}(-i\gamma) \\ \times J_{\sqrt{\lambda_3}} \left( \sqrt{\lambda_2} \rho_n \right) e^{i \sqrt{\lambda_3} \phi_n}$$

Here we have

$$\alpha = \frac{\epsilon M_n \mathcal{E}}{\hbar^2},$$

$$\gamma = \frac{2}{3\alpha} (\lambda_1 + \alpha z_n),$$

$$\lambda = \lambda_1 + \lambda_2,$$

and

$$\lambda = \frac{2M_n}{\hbar^2} (W - E_1).$$

The Bessel functions are as defined by Jahnke and Emde.<sup>22</sup> Note that the  
 normalization factor differs from that of reference 1 by a factor  $2^{1/6}$ .

For well-behaved solutions, we must have  $\lambda_2 \geq 0$ , therefore we have

$$\lambda_1 \leq \lambda.$$

Using these wave functions and the exact bound-state wave function,<sup>12</sup>  
 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

$J = \sqrt{\lambda_3} = 0$ . The transition rate is given by

$$N(T) = \frac{2^{1/3} \epsilon^2 \mathcal{E}^2 M_n a_0^3}{16\pi \hbar^3 (3\alpha)^{1/3}} \mu_0,$$

where

$$\mu_0 = \int_0^\infty |\mu_1|^2 d\lambda_2$$

and

$$\mu_1 = \int_{-\infty}^\infty dz' z'^{1/3} i^{2/3} H_{1/3}^{(2)}(-i\gamma) \times \int_0^\infty d\rho' \rho' J_0(\sqrt{\lambda_2} \rho') \frac{\chi_V(r')}{r'}$$

Here we have

$$z' = \frac{z_n}{a_0},$$

$$\rho' = \frac{\rho_n}{a_0},$$

and

$$r'^2 = \rho'^2 + z'^2;$$

$\chi_V(r')/r'^1$  is the radial function of the initial vibrational state.

The functions  $\chi_V(r')$  exist only in numerical form and  $\mu_1$  and  $\mu_0$  must be integrated numerically. The results of these calculations are summarized in Fig. 4, which is a plot of the 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 additional term appearing in Eq. (III.7b) for the perturbed ion,

$$E_g - E_1 = \frac{E_2 - E_1}{2} - \frac{1}{2} \left[ (E_2 - E_1)^2 + 4H_{12}^2 \right]^{\frac{1}{2}},$$

gives rise to a first-order perturbation that has the effect of lowering the unperturbed vibrational states. 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 5 mv. 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 is spherically symmetric and using the one-dimensional WKB barrier-penetration formula,

$$N(T) = 10^{14} e^{-\frac{2}{\hbar} \int_{r_1}^{r_2} \left\{ 2 M_n \left[ W_{lv} - V(r_n) \right] \right\}^{\frac{1}{2}} dr_n},$$

where

$$V(r_n) = \frac{e^2}{r_n} + E_g(r_n, \mathcal{E}).$$

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 non-rotating ( $J = 0$ ) molecular ions. In the more general case the effects of rotation must be considered. The rotational state of the ion will depend primarily on the particular mechanism which led to the formation of the ion. Under typical laboratory conditions the ionization process is induced by a 15-100 e.v. electron impinging on an  $H_2$  molecule which is normally at room temperature. The most probable rotational state of the ion is given by  $J = (M r_n^2 kT/2\hbar^2)^{\frac{1}{2}} - \frac{1}{2}$ . For  $H_2$ ,  $r_n \approx 0.85 \text{ \AA}$ , and at  $T = 300^\circ\text{C}$ , we have  $J \approx 1$ . The orbital angular momentum of the impinging electron is approximately one to five units of  $\hbar$ ; we can suspect then that the molecular ions will also have a distribution of  $J$  values in this range. The correct distribution of these rotational states must come from a detailed study of the ionization process.

If the molecule is rotating the potential function deforms in such a way as to reduce the binding energy of any particular vibrational level. This effect is clearly in the direction of reducing the required field for dissociation. On the other hand, the potential function for dissociation is now deformed in such a way that depending on component of angular momentum along the Z-axis, the dissociation can be inhibited. If  $m$  is the component of orbital angular momentum along the Z-axis, we have, upon examining the asymptotic solution,  $\chi_{AC}$ , the selection rule,  $m = \sqrt{\lambda_3}$ . Examining the matrix element for the transition we see that the primary effect toward reducing the transition rate is contained in the  $J_m \left( \sqrt{\lambda_3} \rho_n \right)$  factor in  $\chi_{AC}$ . The minimum



of the saddle for the non-rotating molecule will occur at  $\rho_n = 0$ . For  $m = 0$  we have

$$J_0 \left( \sqrt{\lambda_2} \rho_n \right) \Big|_{\rho_n \rightarrow 0} = 1 ;$$

for  $m > 0$ , we have

$$J_m \left( \sqrt{\lambda_2} \rho_n \right) \Big|_{\rho_n \rightarrow 0} = \left( \sqrt{\lambda_2} \rho_n \right)^m .$$

Hence for large  $m$  the wave function is suppressed in the region of the potential where the saddle exists for  $m = 0$ ; it is clear that the transition rate is reduced as  $m$  increases. For  $m = 0$  there exists only one saddle at either end of the bound region of the nuclear potential, and located on the Z-axis; for  $m > 0$  these point saddles become ring shaped and located symmetrically about the Z-axis, the distance from the Z-axis and the height of the saddles increasing as  $J$  increases.

As an illustration of the significance of these rotational effects let us compare the fields required for dissociation in  $10^{-8}$  secs. 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 thirty percent less for  $J = 4$  than for  $J = 0$ . The effect of the rotation in raising the vibrational eigenvalue is the dominating factor here. For  $J = 4, m = 4$ , the required for dissociation field is approximately forty percent larger than for  $J = 0$ . We conclude that the presence of rotation has the effect of lowering the threshold 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  $\text{He}_2^+$  ion and the  $\text{Li}_2^+$  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.<sup>23, 24</sup> 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.<sup>25</sup> The general form of the perturbation with which we shall be concerned occurs in the electronic Eq. (II.5) and has the form

$$R = e\mathcal{E} \left[ 1 + \frac{(a + b - n)m}{M_a + M_b + nm} \right] \sum_i^n z_i = \epsilon \mathcal{E} \frac{r}{2} \cos \theta_n \sum_{i=1}^n \eta_i \xi_i \quad (\text{III.8a})$$

Let  $\psi_i$  represent a determinantal function describing the  $i$ th electronic state and  $a_k$  a particular spin orbital in  $\psi_i$ . We have then

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

if  $\psi_j$  and  $\psi_i$  differ by more than one set of quantum numbers, and

$$(\psi_j | R | \psi_i) = \pm \int a_k^*(1) R(1) a_\ell(1) d^3 r_1, \quad (\text{III.9a})$$

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

$$(\psi_j | R | \psi_j) = \sum_{i=1}^n \int a_i^*(1) R(1) a_i(1) d^3 r_1. \quad (\text{III.9b})$$

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  $\sum_g^1$  state.

The wave function for this ground state is given by

$$\psi_1 = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) \alpha(1) & \psi_1(2) \alpha(2) \\ \psi_1(1) \beta(1) & \psi_1(2) \beta(2) \end{vmatrix}$$

The  $\alpha$ 's and  $\beta$ 's are the conventional spin functions, and the  $\psi_1$  function is of the form given in Eq. (III 2,b). 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  $\psi_1$  and the first excited

orbital,  $\psi_2$  are each occupied. Hund's rule calls for a spin-one state. The wave function for this  $\sum_{\mu}^3$  antibonding state is given by

$$\psi_2 = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_1(1) \alpha(1) & \psi_1(2) \alpha(2) \\ \psi_2(1) \alpha(1) & \psi_2(2) \alpha(2) \end{vmatrix}$$

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

$$H_{11} = \left( \psi_1 \left| e\mathcal{E} \frac{r}{2} \cos \theta_n (\eta_1 \xi_1 + \eta_2 \xi_2) \right| \psi_1 \right) + E_1 = 0 + E_1 = E_1,$$

$$H_{22} = \left( \psi_2 \left| e\mathcal{E} \frac{r}{2} \cos \theta_n (\eta_1 \xi_1 + \eta_2 \xi_2) \right| \psi_2 \right) + E_2 = 0 + E_2 = E_2,$$

and

$$H_{12} = H_{21} = \left( \psi_2 \left| e\mathcal{E} \frac{r}{2} \cos \theta_n [\eta_1 \xi_1 + \eta_2 \xi_2] \right| \psi_1 \right) = 0.$$

For homonuclear molecules the diagonal terms will always be unperturbed, since the perturbation is an odd function. The  $H_{12}$  term vanishes both because of the orthogonality of the spin functions and the cancellation of the orbital integrals. This result could have been obtained immediately by noting that  $\psi_2$  and  $\psi_1$  differ by two sets of quantum numbers and invoking the first of Eq. (III.9a). 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. If we use Oppenheimer's result that no appreciable dissociation of the H atom

occurs unless the field value is of order  $10^8$  v/cm together with the general observation that the necessary field for dissociation is roughly proportional to the electronic eigenvalue, we can estimate the field required to dissociate the molecule in terms of the value required to dissociate the atom. In the atomic case, the appropriate origin of the electronic potential function is the nucleus, whereas for the homonuclear molecule, the appropriate origin is at the center of the two nuclei. The effect of the electric field in inducing electron stripping is therefore magnified for the molecular case over the atomic case. If  $r_{nc}$  is the outer classical turning point of a particular molecular vibrational state of the molecule in question, the electric field required to strip an electron from the molecule compared with the atom is reduced by the factor  $\left[ \frac{r_{nc}}{2 a_0} E_1(\infty) \right] / \left[ 2 a_0 E_1(r_{nc}) \right]$ .

Note that an uppermost vibrational level of sufficiently small binding energy may become unstable prior to electron stripping because of the higher-order effects [Eq. (III.6d)].

The above argument for  $H_2$  is readily generalized to any neutral homonuclear molecule that has a  $\sum_g^{l+}$  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.9a) we have our result. For those molecules that do not have a  $\sum_g^{l+}$  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.9a). 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

$$-\frac{1}{2} \epsilon \mathcal{E} r_n | \cos \theta_n |.$$

It is interesting to apply these conclusions to the  $Li_2^+$  ion. Here the equilibrium internuclear separation is three times as large as for  $H_2^+$  (i.e., 3 angströms) and the potential depth is one-half that of  $H_2^+$ . For the ground vibrational state, the necessary field for dissociation is therefore approximately one-sixth that required for dissociating the ground state of  $H_2^+$ . From Fig. 4 we see that the required field for dissociating an  $H_2^+$  ion in its ground vibrational state is approximately  $2 \times 10^8$  v/cm; therefore we estimate the required field for dissociating the ground state of  $Li_2^+$  to be approximately  $3 \times 10^7$  v/cm. The potential function for large internuclear separations is not known, but for a vibrational state near the top of the potential well a field of one-third to one-fourth that required to dissociate a corresponding upper level in  $H_2^+$  is estimated. The alkali ions --  $Li_2^+$ ,  $Na_2^+$ ,  $K_2^+$ , etc. -- are all apparently relatively susceptible to dissociation, since their respective neutral molecules are characterized by large equilibrium configurations and shallow potential minima.<sup>26</sup>

(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.9a) 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.4) 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  $-e \mathcal{E} \left[ \frac{aM_b - bM_a}{M_a + M_b} \right] z_n$  contained in the nuclear Eq. (II.5).

##### (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  $\lambda, \mu$  must be followed by a translation along the internuclear axis.

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

$$\epsilon \mathcal{E} z_1 = \epsilon \mathcal{E} \left[ x'_1 \sin \lambda + y'_1 \sin \mu \cos \lambda + z'_1 \cos \mu \cos \lambda \right].$$

If  $z_0$  is the position of the center of mass with respect to the origin of the  $x'', y'', z''$  system, we have  $z_0 = (r_n/2) \left[ \frac{M_a - M_b}{M_a + M_b} \right]$ . The perturbation in the  $x'', y'', z''$  frame is then

$$\epsilon \mathcal{E} z_1 = e \mathcal{E} \left[ x''_1 \sin \lambda + y''_1 \sin \mu \cos \lambda + (z'' - z_0) \cos \lambda \cos \mu \right].$$

The terms in  $x''$  and  $y''$  will vanish under the  $\varphi$  integration as before. Our relevant perturbation term expressed in the  $\eta, \xi, \varphi$  coordinates is now written as

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

In the limit of large internuclear separation, the ground electronic state of the unperturbed  $\text{HD}^+$  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<sup>15</sup>

$$\begin{aligned} \psi_b &= A_b \left[ \cos h \frac{Q_1 \eta}{2} e^{-P_1 \xi/2} - \sin h \frac{Q_2 \eta}{2} e^{-P_2 \xi/2} \right], \\ \psi_a &= A_a \left[ \cos h \frac{Q_1 \eta}{2} e^{-P_1 \xi/2} + \sin h \frac{Q_2 \eta}{2} e^{-P_2 \xi/2} \right]. \end{aligned} \quad (\text{III.10a})$$



In the limit as  $r_n$  goes to  $\infty$ , we have  $A_b = A_a = \frac{1}{\sqrt{\pi}}$ , and

$$\psi_b \rightarrow \frac{1}{\sqrt{\pi}} e^{-r_b},$$

and

$$\psi_a \rightarrow \frac{1}{\sqrt{\pi}} e^{-r_a}. \quad (\text{III.10b})$$

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 submatrix analogous to matrix (III.4). The matrix elements are now:

$$\begin{aligned} H_{11} &= \left( \psi_b \left| \varepsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n \left[ \eta_1 \xi_1 - \left( \frac{M_a - M_b}{M_a + M_b} \right) \right] \right| \psi_b \right) + E_1 \\ &= \varepsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n \left\{ A_b^2 \frac{r_n^4}{4} \left[ E_{31} C_1 - E_{11} C_3 - 2 (D_1 E_{312} - D_3 E_{112}) + \right. \right. \\ &\quad \left. \left. + E_{32} B_1 - B_3 E_{12} \right] - \left( \frac{M_a - M_b}{M_a + M_b} \right) \right\} + E_1 \\ &= \varepsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n \left\{ A_b^2 \frac{r_n^4}{2} \left[ D_3 E_{112} - D_1 E_{312} \right] - \left( \frac{M_a - M_b}{M_a + M_b} \right) \right\} + E_1 ; \\ H_{22} &= \left( \psi_a \left| \varepsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n \left[ \eta_1 \xi_1 - \left( \frac{M_a - M_b}{M_a + M_b} \right) \right] \right| \psi_a \right) + E_2 \\ &= \varepsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n \left\{ A_a^2 \frac{r_n^4}{4} \left[ E_{31} C_1 - E_{11} C_3 + 2 (D_1 E_{312} - D_3 E_{112}) + \right. \right. \\ &\quad \left. \left. + E_{32} F_1 - F_3 E_{12} \right] - \left( \frac{M_a - M_b}{M_a + M_b} \right) \right\} + E_2 \\ &= \varepsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n \left\{ A_a^2 \frac{r_n^4}{2} \left[ D_1 E_{312} - D_3 E_{112} \right] - \left( \frac{M_a - M_b}{M_a + M_b} \right) \right\} + E_2 ; \\ H_{12} = H_{21} &= \left( \psi_a \left| \varepsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n \left[ \eta_1 \xi_1 - \left( \frac{M_a - M_b}{M_a + M_b} \right) \right] \right| \psi_b \right) \\ &= \varepsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n \left\{ A_a A_b \frac{r_n^4}{4} \left[ E_{31} C_1 - E_{11} C_3 + E_{32} B_1 - B_3 E_{12} \right] \right\} = 0. \end{aligned} \quad (\text{III.11a})$$

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

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

and

$$H_{22} \rightarrow +\frac{2}{3} \epsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n + E_2. \quad (\text{III.11b})$$

If we combine Eq. (III.11b) with the term  $-\epsilon \mathcal{E} \left[ \frac{aM_b - bM_a}{M_a + M_b} \right] z_n$  which occurs explicitly in the nuclear Eq. (II.5), the asymptotic potentials for the nuclear motion are given by

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

and

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

These potentials are illustrated in Fig. 6. It is clear that, in the "classical" limit, the  $\text{HD}^+$  ion is more susceptible to dissociation than is  $\text{H}_2^+$ . One can readily show that, for the  $\text{HT}^+$  ion, the coefficients in the asymptotic nuclear potential are  $-3/4$  and  $+1/4$ , respectively.

## (2) Dissociation of HD

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

$$\psi_G = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_a(1) \alpha(1) & \psi_a(2) \beta(2) \\ \psi_b(1) \alpha(1) & \psi_b(2) \beta(2) \end{vmatrix}.$$

The pertinent matrix element is written

$$H_{11} = \left( \psi_G \left| \epsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n \right| \xi_1 \eta_1 + \xi_2 \eta_2 - 2 \left( \frac{M_a - M_b}{M_a + M_b} \right) \left| \psi_G \right) + E_1.$$

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

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

If we use the results obtained for  $\text{HD}^+$ , 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.

One can readily show that had we chosen for our ground-state wave function a Heitler-London function,

$$\psi_g = \frac{1}{2} \left[ \psi_a(1) \psi_b(2) + \psi_a(2) \psi_b(1) \right] \left[ \alpha(1) \beta(1) - \alpha(2) \beta(2) \right] ,$$

an identical result would have been obtained.

### (3) Dissociation of $\text{LiH}^+$

The ground state of the  $\text{LiH}$  molecule has a large equilibrium separation and a relatively shallow potential minimum. No data exist on the properties of  $\text{LiH}^+$  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  $\text{Li H}^+$  consists of two occupied  $\psi_b$  orbitals and one  $\psi_a$  orbital.<sup>27</sup> In the limit of large  $r_n$ ,  $\text{LiH}^+ \rightarrow \text{Li}^+ + \text{H}$ . Our ground-state wave function is

$$\psi_g = \frac{1}{\sqrt{31}} \begin{vmatrix} \psi_b(1) \alpha(1) & \psi_b(2) \alpha(2) & \psi_b(3) \alpha(3) \\ \psi_b(1) \beta(1) & \psi_b(2) \beta(2) & \psi_b(3) \beta(3) \\ \psi_a(1) \alpha(1) & \psi_a(2) \alpha(2) & \psi_a(3) \alpha(3) \end{vmatrix} .$$

The matrix element becomes

$$\begin{aligned}
 H_{11} &= \left( \psi_g \left| \epsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n \left[ \xi_1 \eta_1 + \xi_2 \eta_2 + \xi_3 \eta_3 - \right. \right. \right. \\
 &\quad \left. \left. \left. - 3 \left( \frac{M_a - M_b}{M_a + M_b} \right) \right] \right| \psi_2 + E_1 \right) \\
 &= \epsilon \mathcal{E} \frac{r_n}{2} \cos \theta_n \left\{ 2 (\psi_b | \xi_1 \eta_1 | \psi_b) + (\psi_a | \xi_1 \eta_1 | \psi_a) + \frac{9}{4} \right\} + E_1; \\
 H_{11} &\rightarrow \frac{5}{8} \epsilon \mathcal{E} r_n \cos \theta_n + E_1.
 \end{aligned}$$

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

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

#### (4) Dissociation of $\text{LiH}^{++}$

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  $\text{LiH}^+$  illustrates the sensitive dependence of the problem on the charge states of the ion and its dissociation products. The  $\text{LiH}^{++}$  dissociates according to  $\text{LiH}^{++} \rightarrow \text{Li}^+ + \text{H}^+$ . The wave function is now

$$\psi_g = \frac{1}{\sqrt{2}} \begin{vmatrix} \psi_b(1) \alpha(1) & \psi_b(2) \alpha(2) \\ \psi_b(1) \beta(1) & \psi_b(2) \beta(2) \end{vmatrix},$$

and the matrix element is

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

In the limit of large  $r_n$ , we have

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

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

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

The  $\text{Li H}^{++}$  ion is appreciably more susceptible to dissociation than is  $\text{Li H}^+$ . A comparison of the potentials for these two cases is indicated schematically in Fig. 7 in which the asymptotic potentials are drawn for the same electric field value.

### C. Classical Treatment of Dissociation

We conclude Section III with an elementary discussion of the classical dissociation of two charged bodies. Let  $e_A$  and  $e_B$  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:

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

and

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

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:

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

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

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

This relative potential is in agreement with the asymptotic potentials 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. 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  $-1/2 e\mathcal{E} |z_n|$ . 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  $2 \times 10^8$  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 one 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.* has shown that most of the vibrational states of the  $H_2^+$  ion remain populated when such ions are accelerated in Van DeGraaff machines.<sup>28</sup> 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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#### APPENDICES

##### Appendix A

Here we consider the transformation of the term  $V_2$  in Eq. (II.1) into a function of the  $n + 2$  new coordinates which are defined in Eq. (II.2). We have:

$$\begin{aligned}
 V'_2 &= az_a + bz_b - \sum_{i=1}^n z_{ei} = \frac{1}{M_a + M_b + nm} \left[ (M_a + M_b + nm)(az_a + bz_b) \right. \\
 &\quad \left. - (M_a + M_b + nm) \sum_{i=1}^n z_{ei} \right] \\
 &= \frac{1}{M_a + M_b + nm} \left\{ aM_a z_a + bM_b z_b + bM_a z_a + aM_b z_b + nm (az_a + bz_b) \right. \\
 &\quad + (b - n)(M_a z_a + m \sum_{i=1}^n z_{ei}) + (a - n)(M_b z_b + m \sum_{i=1}^n z_{ei}) \\
 &\quad + nm \sum_{i=1}^n z_{ci} \\
 &\quad \left. - \left[ (b - n)(M_a z_a + m \sum_{i=1}^n z_{ei}) + (a - n)(M_b z_b + m \sum_{i=1}^n z_{ei}) \right] - nm \sum_{i=1}^n z_{ei} \right. \\
 &\quad \left. - (M_a + M_b + nm) \sum_{i=1}^n z_{ei} \right\} \\
 &= \frac{1}{M_a + M_b + nm} \left\{ (a + b - n)(M_a z_a + M_b z_b + m \sum_{i=1}^n z_{ei}) \right. \\
 &\quad + bM_a z_b + aM_b z_a + nm (az_a + bz_b) \\
 &\quad \left. - \left[ (b - n)(M_a z_a + m \sum_{i=1}^n z_{ei}) + (a - n)(M_b z_b + m \sum_{i=1}^n z_{ei}) \right] \right. \\
 &\quad \left. - (M_a + M_b + 2nm) \sum_{i=1}^n z_{ei} \right\} \\
 az_a + bz_b - \sum_{i=1}^n z_{ei} &= (a + b - n) z_c + \frac{1}{M_a + M_b + nm} \left\{ bM_a z_b + aM_b z_a + nm (az_a + bz_b) \right. \\
 &\quad \left. - \left[ (b - n)(M_a z_a + m \sum_{i=1}^n z_{ei}) + (a - n)(M_b z_b + m \sum_{i=1}^n z_{ei}) \right] \right. \\
 &\quad \left. - (M_a + M_b + 2nm) \sum_{i=1}^n z_{ei} \right\}.
 \end{aligned}$$

Note that

$$nm(az_a + bz_b) = \frac{nm}{M_a + M_b} (aM_a z_a + bM_b z_b + aM_b z_a + bM_a z_b)$$



and

$$(aM_b - bM_a) \left(1 + \frac{nm}{M_a + M_b}\right) (z_a - z_b) = (aM_b z_a - bM_a z_a - aM_b z_b + bM_a z_b) \left(1 + \frac{nm}{M_a + M_b}\right).$$

Inserting these expressions in the above and expanding some terms, we obtain

$$\begin{aligned} V'_2 = & (a + b - n) z_c + \frac{1}{M_a + M_b + nm} \left\{ bM_a z_b + aM_b z_a + \right. \\ & + \frac{nm}{M_a + M_b} (aM_a z_a + bM_b z_b + aM_b z_a + bM_a z_b) \\ & + (aM_b - bM_a) \left(1 + \frac{nm}{M_a + M_b}\right) (z_a - z_b) \\ & - (aM_b z_a - bM_a z_a - aM_b z_b + bM_a z_b) \left(1 + \frac{nm}{M_a + M_b}\right) \\ & - \left[ bM_a z_a - nM_a z_a + (b - n) m \sum_{i=1}^n z_{ei} \right] \\ & - \left[ aM_b z_b - nM_b z_b + (a - n) m \sum_{i=1}^n z_{ei} \right] \\ & \left. - (M_a + M_b + 2nm) \sum_{i=1}^n z_{ei} \right\}. \end{aligned}$$

If we collect terms, this reduces to

$$\begin{aligned} V'_2 = & (a + b - n) z_c + \frac{1}{M_a + M_b + nm} \left\{ (aM_b - bM_a) \left(1 + \frac{nm}{M_a + M_b}\right) z_n + \right. \\ & + n \left(1 + \frac{(a+b)m}{M_a + M_b}\right) (M_a z_a + M_b z_b) - (a+b)m \sum_{i=1}^n z_{ei} \\ & \left. + 2nm \sum_{i=1}^n z_{ei} - (M_a + M_b + 2nm) \sum_{i=1}^n z_{ei} \right\} \\ = & (a + b - n) z_c + \frac{1}{M_a + M_b + nm} \left\{ (aM_b - bM_a) \left(1 + \frac{nm}{M_a + M_b}\right) z_n \right. \\ & + (M_a + M_b) \left[ n \left(1 + \frac{(a+b)m}{M_a + M_b}\right) \frac{M_a z_a + M_b z_b}{M_a + M_b} \right. \\ & \left. \left. - \left(1 + \frac{(a+b)m}{M_a + M_b}\right) \sum_{i=1}^n z_{ei} \right] \right\} \end{aligned}$$

$$= (a + b - n) z_c + \left( \frac{aM_b - bM_a}{M_a + M_b} \right) z_n$$

$$+ \frac{M_a + M_b + (a + b)m}{M_a + M_b + nm} \left[ n \frac{(M_a z_a + M_b z_b)}{M_a + M_b} - \sum_{i=1}^n z_{ei} \right]$$

Finally, we have

$$az_a + bz_b - \sum_{i=1}^n z_{ei} = (a+b-n)z_c + \left( \frac{aM_b - bM_a}{M_a + M_b} \right) z_n - \left[ 1 + \frac{(a+b-n)m}{M_a + M_b + nm} \right] \sum_{i=1}^n z_i$$

### Appendix B

In this appendix we consider the electromagnetic transitions of the general diatomic molecule. We shall be concerned both with spontaneous electromagnetic transitions and transitions induced by switching on the electrostatic field.

#### A. Spontaneous Transitions

The Hamiltonian for the general diatomic molecule in the presence of an electromagnetic field described by the potential  $\vec{A}$  is given by

$$\left[ \frac{1}{2M_a} (\vec{p}_a - \frac{ea}{c} \vec{A}_a)^2 + \frac{1}{2M_b} (\vec{p}_b - \frac{eb}{c} \vec{A}_b)^2 + \frac{1}{2m} \sum_{i=1}^n (\vec{p}_{ei} + \frac{e}{c} \vec{A}_{ei})^2 + V_1 \right] \psi = - \frac{\hbar}{i} \frac{\partial}{\partial t} \psi,$$

where

$$\vec{A}_a = \vec{A}_0 e^{i\vec{k} \cdot \vec{r}_a}, \text{ etc.}$$

If we expand the brackets, use  $\vec{A} \cdot \vec{p} - \vec{p} \cdot \vec{A} = -\hbar/i \nabla \cdot \vec{A}$ , set  $\vec{\nabla} \cdot \vec{A} = 0$ , and neglect terms of order  $\vec{A}^2$ , this reduces to

$$\left[ - \frac{\hbar^2}{2} \left( \frac{1}{M_a} \nabla_a^2 + \frac{1}{M_b} \nabla_b^2 + \frac{1}{m} \sum_{i=1}^n \nabla_{ei}^2 \right) + V_1 \right.$$

$$\left. - \frac{e\hbar}{ic} \left( \frac{a}{M_a} \vec{A}_a \cdot \nabla_a + \frac{b}{M_b} \vec{A}_b \cdot \nabla_b - \frac{1}{m} \sum_{i=1}^n \vec{A}_{ei} \cdot \nabla_{ei} \right) \right] \psi = - \frac{\hbar}{i} \frac{\partial}{\partial t} \psi.$$

Introducing the transformation given in Eq. (II.2) and writing  $H_0$  for the Hamiltonian when  $\vec{A} = 0$ , we have

$$\vec{\nabla}_a = \rho_a \vec{\nabla}_c + \vec{\nabla}_n - f_a \sum_i^n \vec{\nabla}_i,$$

$$\vec{\nabla}_b = \rho_b \vec{\nabla}_c - \vec{\nabla}_n - f_b \sum_i^n \vec{\nabla}_i,$$

and

$$\vec{\nabla}_{ei} = \rho \vec{\nabla}_c + \vec{\nabla}_i,$$

which gives

$$\begin{aligned} \left[ H_0 - \frac{e\hbar}{ic} \left( \frac{a\rho}{M_a} \vec{A}_a + \frac{b\rho_b}{M_b} \vec{A}_b - \frac{n\rho}{m} \vec{A}_{ei} \right) \cdot \vec{\nabla}_c \right. \\ \left. - \frac{e\hbar}{ic} \left( \frac{a}{M_a} \vec{A}_a - \frac{b}{M_b} \vec{A}_b \right) \cdot \vec{\nabla}_n \right. \\ \left. + \frac{e\hbar}{ic} \sum_{i=1}^n \left( \frac{af_a}{M_a} \vec{A}_a + \frac{bf_b}{M_b} \vec{A}_b - \frac{1}{m} \vec{A}_{ei} \right) \cdot \vec{\nabla}_i \right] \psi = - \frac{\hbar}{i} \frac{\partial}{\partial t} \psi. \end{aligned}$$

We are concerned with transitions between the various vibrational states belonging to the same electronic state and, in particular, with those of the lowest electronic state. The initial state is given by

$$\psi = \pi(\vec{r}_c, E_c) \psi_1(\vec{r}_n, \vec{r}_i, E_1) \chi_{1j}(\vec{r}_n, W_j),$$

and the final state by

$$\psi = \pi(\vec{r}_c, E_c) \psi_1(\vec{r}_n, \vec{r}_i, E_1) \chi_{1k}(\vec{r}_n, W_k).$$

In a dipole approximation we set  $e^{i\vec{k} \cdot \vec{r}} = 1$ . The contributions from  $\vec{\nabla}_c$  and  $\vec{\nabla}_i$  vanish. Upon examining Heitler's<sup>29</sup> formulae (2) and (12) and dividing formula (12) by  $\sqrt{V_{kj}}$ , we have for the transition

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

For homonuclear molecules this transition rate is zero and we require the quadrupole terms. For homonuclear molecules we have, from transformation (II.2),

$$\vec{r}_a = \left(2 + \frac{nm}{M}\right)^{-1} \left[ \left(1 + \frac{nm}{2M}\right) \vec{r}_n + \left(2 + \frac{nm}{M}\right) \vec{r}_c - \frac{m}{M} \sum_i^n \vec{r}_i \right],$$

$$\vec{r}_b = \left(2 + \frac{nm}{M}\right)^{-1} \left[ -\left(1 + \frac{nm}{2M}\right) \vec{r}_n + \left(2 + \frac{nm}{M}\right) \vec{r}_c - \frac{m}{M} \sum_i^n \vec{r}_i \right],$$

$$\vec{r}_e = \left(1 + \frac{nm}{2M}\right)^{-1} \left[ \vec{r}_i + \vec{r}_c \right].$$

Neglecting terms of order  $nm/M$  compared with unity, these reduce to

$$\vec{r}_a = \frac{1}{2} \vec{r}_n + \vec{r}_c - \frac{m}{2M} \sum_i^n \vec{r}_i,$$

$$\vec{r}_b = -\frac{1}{2} \vec{r}_n + \vec{r}_c - \frac{m}{2M} \sum_i^n \vec{r}_i,$$

and

$$\vec{r}_{ei} = \vec{r}_i + \vec{r}_c.$$

We have then

$$\vec{A}_a = \vec{A}_0 e^{i \vec{k} \cdot \vec{r}_a} = \vec{A}_0 e^{i \left( \vec{k} \cdot \vec{r}_c - \frac{m}{n} \sum_{i=1}^n \vec{k} \cdot \vec{r}_i \right)} e^{i \frac{1}{2} \vec{k} \cdot \vec{r}_n},$$

$$\vec{A}_b = \vec{A}_0 e^{i \vec{k} \cdot \vec{r}_b} = \vec{A}_0 e^{i \left( \vec{k} \cdot \vec{r}_c - \frac{m}{2M} \sum_{i=1}^n \vec{k} \cdot \vec{r}_i \right)} e^{-i \frac{1}{2} \vec{k} \cdot \vec{r}_n},$$

and

$$\vec{A}_{ei} = \vec{A}_0 e^{i \vec{k} \cdot \vec{r}_{ei}} = \vec{A}_0 e^{i \left( \vec{k} \cdot \vec{r}_i + \vec{k} \cdot \vec{r}_c \right)}.$$

The contributions from the terms in  $\vec{\nabla}_c$  and  $\vec{\nabla}_i$  in the matrix element will again vanish. Writing

$$e^{i \frac{1}{2} \vec{k} \cdot \vec{r}_n} = 1 + \frac{i}{2} \vec{k} \cdot \vec{r}_n,$$

we have for the term in  $\vec{\nabla}_n$  :

$$-\frac{e\hbar}{iM_n c} \left( \frac{a\vec{i}}{2} \cdot \vec{k} \cdot \vec{r}_n \right) \vec{A}_0 e^{i \left( \vec{k} \cdot \vec{r}_c - \frac{m}{2M} \sum_{i=1}^m \vec{k} \cdot \vec{r}_i \right)} \cdot \vec{\nabla}_n$$

The factor  $e^{i(\quad)}$  cancels with its complex conjugate in the evaluation of the matrix element, and using Heitler's formula (22), we have for the transition rate for quadrupole transitions

$$T_Q = \frac{4}{3} \frac{e^2}{c^3} \frac{v_{kj}^3}{\hbar} \left( \frac{a}{2} \right)^2 \left| \langle \chi_k | \vec{r}_n (\vec{k} \cdot \vec{r}_n) | \chi_j \rangle \right|^2$$

### B. Induced Transitions

In the presence of the electrostatic field, the electron cloud is polarized. This polarization is a function of the internuclear separation. As the molecule vibrates this variable polarization can induce a transition between the vibrational states.

For values of the internuclear separation close to the equilibrium separation, the electronic eigenvalue is given approximately by

$$E_g = E_1 - \frac{H_{12}^2}{E_2 - E_1}$$

The electronic wave function corresponding to this state is then

$$\psi_g = \psi_1 - \frac{H_{12}}{E_2 - E_1} \psi_2$$

The initial state of our molecular system is now given by

$$\psi_i = \pi(\vec{r}_c, E_c) \psi_g(\vec{r}_n, \vec{r}_i, E_1) \chi_{lj}(\vec{r}_n, W_j),$$

and the final state by

$$\psi_f = \pi(\vec{r}_c, E_c) \psi_g(\vec{r}_n, \vec{r}_i, E_1) \chi_{lk}(\vec{r}_n, W_k).$$

Using these wave functions, we proceed as in the previous section; the transition of interest is given by the electronic terms in  $\vec{\nabla}_i$

in dipole approximation. Neglecting terms of order  $m/M$  compared with unity, we write the interaction term

$$H_{\text{int}} = - \frac{e\hbar}{imc} \sum_{i=1}^n \vec{A}_{ei} \cdot \vec{\nabla}_i$$

Using previous theorems on determinantal wave functions and taking  $\psi_1$  and  $\psi_2$  as the first and second electronic orbitals, respectively, the pertinent matrix element is written

$$\begin{aligned} (\psi_{gk} | H_{\text{int}} | \psi_{gj}) &= (\psi_1 X_k | H_{\text{int}} | \psi_1 X_j) + \left( \frac{H_{12}}{E_1 - E_2} \psi_2 X_k | H_{\text{int}} | \psi_1 X_j \right) \\ &+ \left( \psi_1 X_k | H_{\text{int}} | \frac{H_{12}}{E_1 - E_2} \psi_2 X_j \right) \\ &+ \left( \frac{H_{12}}{E_1 - E_2} \psi_2 X_k | H_{\text{int}} | \frac{H_{12}}{E_1 - E_2} \psi_2 X_j \right) \end{aligned}$$

The first and fourth terms vanish in the electronic integration; the second and third terms are equal. For the evaluation of the electronic integral, we write

$$\frac{\hbar}{im} (\vec{\nabla}_i)_{21} = iV_{21}(r_1)_{21} = i \left( \frac{E_2 - E_1}{\hbar} \right) (r_1)_{21}$$

The transition rate becomes

$$T_1 = \frac{4}{3} \frac{e^2}{c^3} \frac{V_{ij}}{\hbar} \left[ \left( \frac{2}{E_2 - E_1} \right) \left( \frac{E_2 - E_1}{\hbar} \right) \right]^2 \left| (\psi_2 X_k | r_1 H_{12} | \psi_1 X_j) \right|^2$$

For homonuclear molecules in the upper vibrational states, we have, approximately,  $H_{12} = 1/2 e \mathcal{E} r_n \cos \theta_n$ ; the transition rate then reduces to

$$T_1 = \frac{4}{3} \frac{e^4}{c^3} \frac{V_{jk} \mathcal{E}^2}{\hbar^3} \left| (\psi_2 X_k | r_1 r_n \cos \theta_n | \psi_1 X_j) \right|^2$$

The transition rate given in reference 10 is in error. The selection rules for these transitions have been discussed previously by Condon.<sup>16</sup>

Appendix C

In this appendix various integrals encountered in Section III are defined and evaluated as follows:

$$E_{0n} = \int_1^{\infty} e^{-P_n \xi} d\xi = \frac{1}{P_n} e^{-P_n}$$

$$E_{1n} = \int_1^{\infty} \xi e^{-P_n \xi} d\xi = \frac{e^{-P_n}}{P_n^2} (P_n + 1)$$

$$E_{2n} = \int_1^{\infty} \xi^2 e^{-P_n \xi} d\xi = \frac{e^{-P_n}}{P_n^3} [P_n^2 + 2(P_n + 1)]$$

$$E_{3n} = \int_1^{\infty} \xi^3 e^{-P_n \xi} d\xi = \frac{e^{-P_n}}{P_n^4} [P_n^3 + 3P_n^2 + 6(P_n + 1)]$$

$$E_{112} = \int_1^{\infty} \xi e^{-\frac{1}{2}(P_1 + P_2)\xi} d\xi = \frac{e^{-\frac{1}{2}(P_1 + P_2)}}{\left[\frac{1}{2}(P_1 + P_2)\right]^2} \left[\frac{1}{2}(P_1 + P_2) + 1\right]$$

$$E_{312} = \int_1^{\infty} \xi^3 e^{-\frac{1}{2}(P_1 + P_2)\xi} d\xi = \frac{e^{-\frac{1}{2}(P_1 + P_2)}}{\left[\frac{1}{2}(P_1 + P_2)\right]^4}$$

$$\times \left[ \frac{1}{8}(P_1 + P_2)^3 + \frac{3}{4}(P_1 + P_2)^2 + 6\left(\frac{1}{2}(P_1 + P_2) + 1\right) \right]$$

$$B_1 = \int_{-1}^{+1} \eta \sinh \frac{Q\eta}{2} \cosh \frac{Q\eta}{2} d\eta = \frac{1}{Q} (\cosh Q - \frac{1}{Q} \sinh Q)$$

$$B_3 = \int_{-1}^{+1} \eta^3 \sinh \frac{Q\eta}{2} \cosh \frac{Q\eta}{2} d\eta$$

$$= \frac{16}{Q^4} \left( \frac{Q^3}{16} \cosh Q - \frac{3}{16} Q^2 \sinh Q + \frac{3}{8} Q \cosh Q - \frac{3}{8} \sinh Q \right)$$

$$C_1 = \int_{-1}^{+1} \eta \cosh^2 \frac{Q\eta}{2} d\eta = 0$$

$$C_2 = \int_{-1}^{+1} \cosh^2 \frac{Q\eta}{2} \eta^2 d\eta = \frac{1}{Q} \left( 2 \sinh \frac{Q}{2} \cosh \frac{Q}{2} + Q \right)$$

$$- \frac{2}{3} - \frac{2}{Q^2} \cosh Q + \frac{2}{Q^3} \sinh Q$$

$$C_3 = \int_{-1}^{+1} \eta^3 \cosh \frac{Q\eta}{2} d\eta = 0$$

$$D_1 = \int_{-1}^{+1} \eta \sinh \frac{Q_2 \eta}{2} \cosh \frac{Q_1 \eta}{2} d\eta = 4 Q_1 \sinh \frac{Q_2}{2} \sinh \frac{Q_1}{2}$$

$$- 4 Q_2 \cosh \frac{Q_2}{2} \cosh \frac{Q_1}{2} + \frac{8}{(Q_2^2 - Q_1^2)(Q_1^2 - Q_2^2)}$$

$$\times \left[ (Q_1^2 + Q_2^2) \sinh \frac{Q_2}{2} \cosh \frac{Q_1}{2} - 2 Q_1 Q_2 \cosh \frac{Q_2}{2} \sinh \frac{Q_1}{2} \right]$$

$$D_3 = \int_{-1}^1 \eta^3 \sinh \frac{Q_2 \eta}{2} \cosh \frac{Q_1 \eta}{2} d\eta$$

$$= \frac{4}{Q_1^2 - Q_2^2} \left[ \frac{Q_2 Q_1 - Q_2^2 Q_1 + 24 Q_2}{(Q_1 - Q_2)^2} \sinh \frac{Q_2}{2} \sinh \frac{Q_1}{2} \right]$$

$$- \frac{4}{Q_1^2 - Q_2^2} \left[ \frac{Q_2 (Q_1 - Q_2)^2 + 24 Q_2}{(Q_1 - Q_2)^2} \cosh \frac{Q_2}{2} \cosh \frac{Q_1}{2} \right]$$

$$- \frac{24}{Q_1^2 - Q_2^2} \left[ \frac{Q_2 (Q_1 - Q_2)^2 + 12 Q_2}{(Q_1 - Q_2)^3} \sinh \frac{Q_2}{2} \cosh \frac{Q_1}{2} \right]$$

$$+ \frac{24}{Q_1^2 - Q_2^2} \left[ \frac{Q_2 (Q_1 - Q_2)^2 + 12 Q_2}{(Q_1 - Q_2)^3} \cosh \frac{Q_2}{2} \sinh \frac{Q_1}{2} \right]$$

$$F_1 = \int_{-1}^1 \eta \sinh^2 \frac{Q\eta}{2} d\eta = 0$$

$$F_3 = \int_{-1}^1 \eta^3 \sinh^2 \frac{Q\eta}{2} d\eta = 0$$



Appendix D

In this appendix we consider the equations of motion of an  $H_2^+$  ion moving in a uniform magnetic field. Our purpose is to inquire 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  $\vec{A} = A_\phi \hat{\phi} = (H/2) \rho \hat{\phi}$ , where  $\rho = (x^2 + y^2)^{1/2}$ . The form of the Hamiltonian for this system is given in part A of Appendix B. Expanding the terms as before, we have

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

The  $x$  and  $y$  components of  $\vec{A}$  are given by

$$A_x = -A_\phi \sin \phi = -\frac{H}{2} y$$

and

$$A_y = A_\phi \cos \phi = \frac{H}{2} x.$$

Using the expressions for  $\vec{r}_a$ ,  $\vec{r}_b$ , and  $\vec{r}_e$  given in Appendix B, we can write the various terms:

$$\begin{aligned} I = & -\frac{e\hbar}{iMc} (\vec{A}_a \cdot \vec{\nabla}_a + \vec{A}_b \cdot \vec{\nabla}_b) = \frac{eH\hbar}{2iMc} \left[ \left( y_c \frac{\partial}{\partial x_c} - x_c \frac{\partial}{\partial y_c} \right) \right. \\ & + \left( x_c \frac{\partial}{\partial y_1} - y_c \frac{\partial}{\partial x_1} \right) + \left( y_n \frac{\partial}{\partial x_n} - x_n \frac{\partial}{\partial y_n} \right) + \frac{m}{2M} \left( x_1 \frac{\partial}{\partial y_c} - y_1 \frac{\partial}{\partial x_c} \right) \\ & \left. + \frac{m}{2M} \left( y_1 \frac{\partial}{\partial x_1} - x_1 \frac{\partial}{\partial y_1} \right) \right] \end{aligned}$$

$$\begin{aligned} \text{II} = \frac{e\hbar}{imc} \vec{A}_e \cdot \vec{P}_e = \frac{eH\hbar}{2imc} & \left[ \frac{m}{2M} \left( x_1 \frac{\partial}{\partial y_c} - y_1 \frac{\partial}{\partial x_c} \right) + \left( x_c \frac{\partial}{\partial y_1} - y_c \frac{\partial}{\partial x_1} \right) \right. \\ & \left. + \left( x_1 \frac{\partial}{\partial y_1} - y_1 \frac{\partial}{\partial x_1} \right) + \frac{m}{2M} \left( x_c \frac{\partial}{\partial y_c} - y_c \frac{\partial}{\partial x_c} \right) \right]. \end{aligned}$$

Combining these expressions and neglecting terms of order  $m/M$  compared with unity, we have

$$\begin{aligned} \text{I} + \text{II} = \frac{eH\hbar}{2Mc^2} & \left[ \frac{1}{2} \frac{\partial}{\partial \phi_c} + \frac{\partial}{\partial \phi_n} + \frac{1}{2} \left( x_1 \frac{\partial}{\partial y_c} - y_1 \frac{\partial}{\partial x_c} \right) \right] \\ & + \frac{eH\hbar}{2mic} \left[ \frac{\partial}{\partial \phi_1} + \left( x_c \frac{\partial}{\partial y_1} - y_c \frac{\partial}{\partial x_1} \right) \right]. \end{aligned}$$

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

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

The second term in  $\text{I} + \text{II}$  is the Zeeman term in the nuclear coordinates and is equal to  $\frac{eH}{2Mc} \hbar (J(J+1))^{\frac{1}{2}}$ , 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

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

where  $\omega = eH/2Mc$ .

Consider next a transformation into a rotating coordinate system:

$$x'_1 = x_1 \cos \omega t + y_1 \sin \omega t$$

$$y'_1 = y_1 \cos \omega t - x_1 \sin \omega t$$

$$z'_1 = z_1$$

and

$$x'_n = x_n \cos \omega t + y_n \sin \omega t$$

$$y'_n = y_n \cos \omega t - x_n \sin \omega t$$

$$z'_n = z_n$$

The third term becomes  $-eH/2c v_c y'_1$ . The electronic and nuclear equations are now written, respectively:

$$\left[ -\frac{\hbar^2}{2m} \nabla_1'^2 - \left( E_K + \frac{e^2}{|\vec{r}'_1 - \frac{1}{2} \vec{r}'_n|} + \frac{e^2}{|\vec{r}'_1 + \frac{1}{2} \vec{r}'_n|} + \frac{eH}{2c} v_c y'_1 \right) \right] \psi_K = 0$$

$$-\frac{\hbar^2}{2M} \nabla_n'^2 + \left[ \frac{e^2}{|r_n|} + E_K(r_n) - W \right] \chi_K = 0$$

If we set  $\mathcal{E} = Hv_c/c$ , these equations have the same form as those considered in part 1 of Section III.

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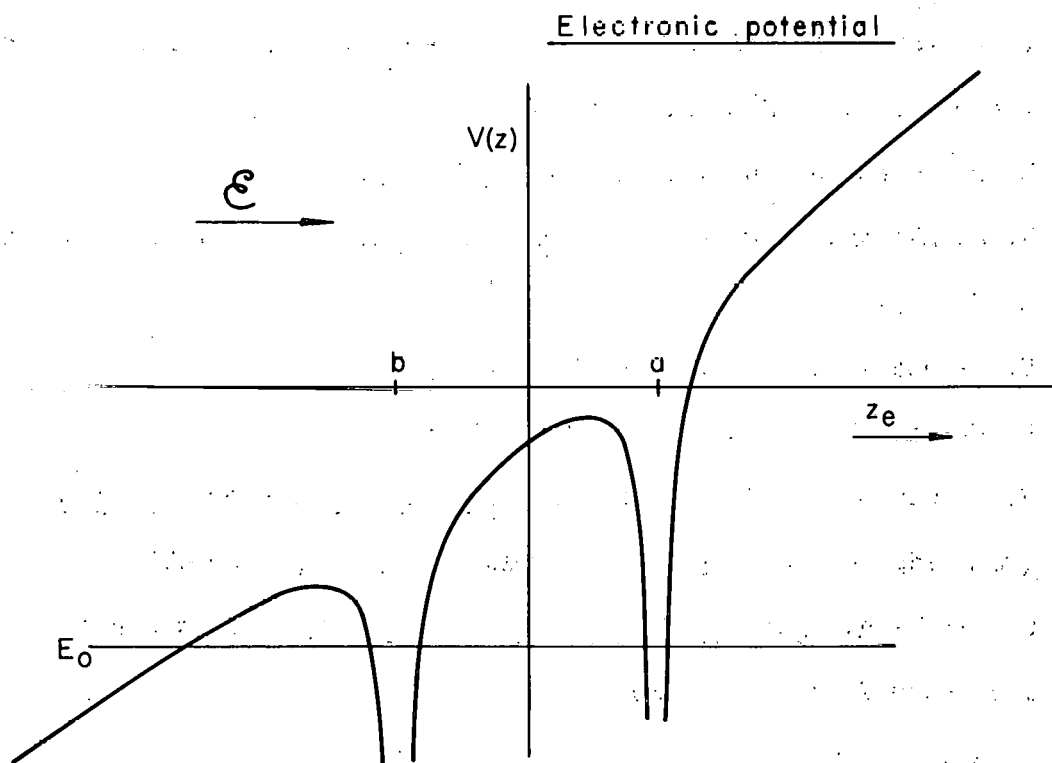
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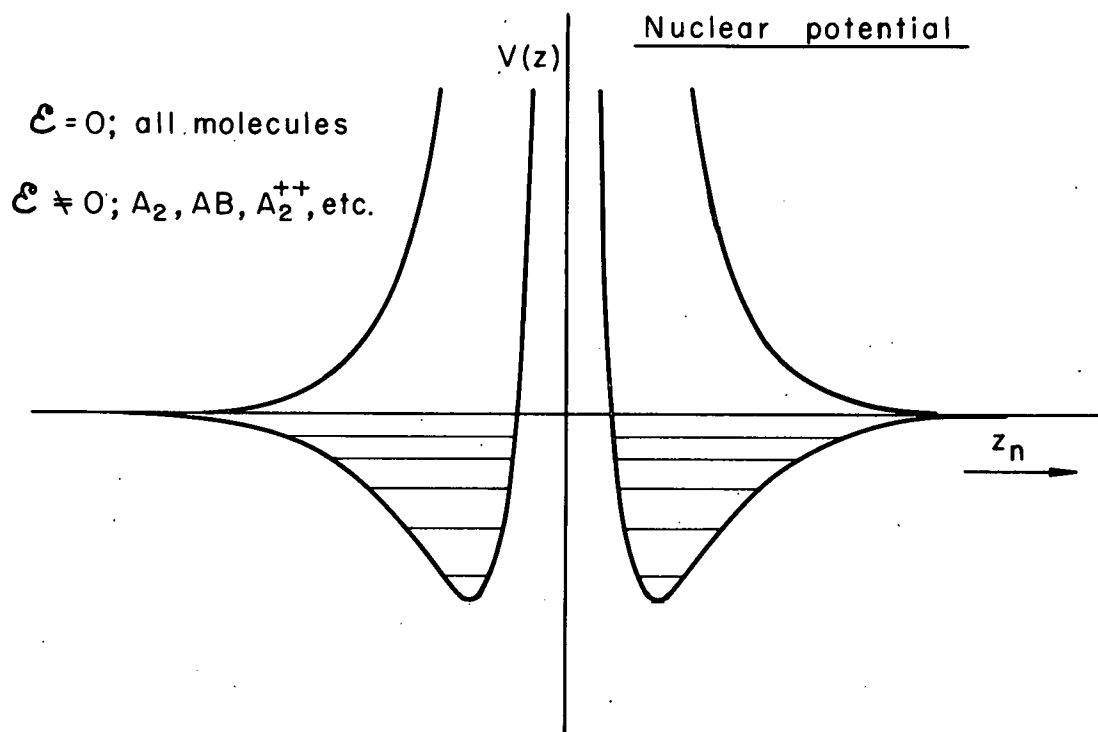
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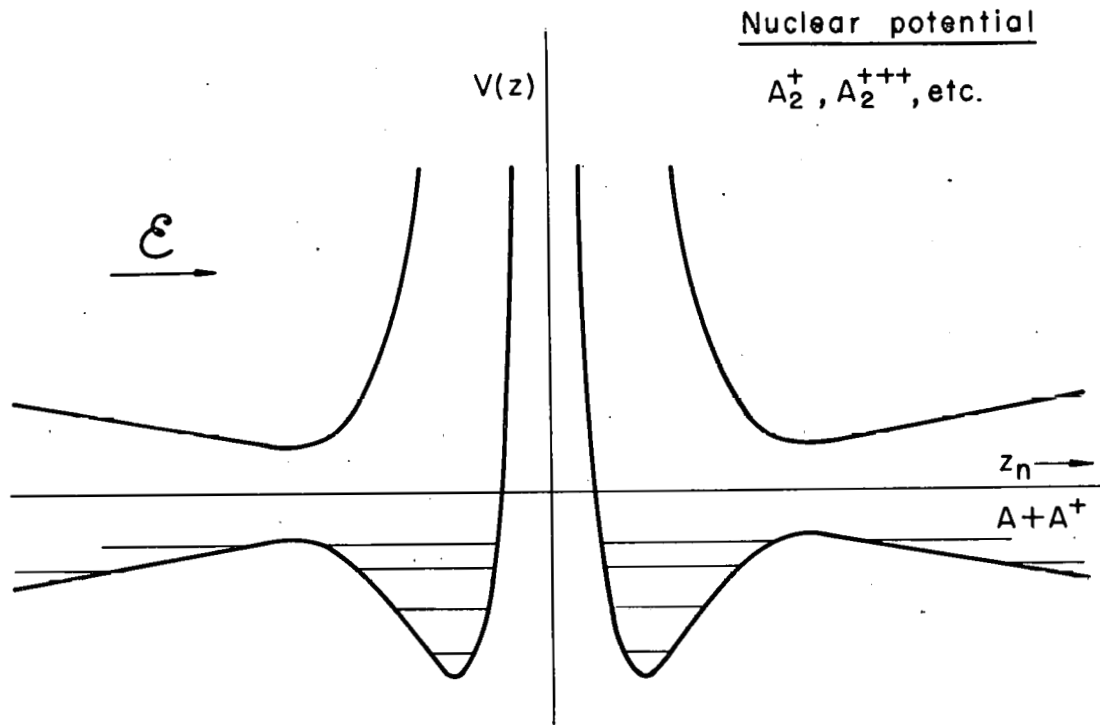
MU-20332

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.



MU - 20333

Fig. 2. The nuclear potential for a diatomic molecular system in the absence of an electric field. Usually this potential is drawn in a spherical-coordinate system, but for the purposes of this paper a cylindrical-coordinate system is more appropriate. The vibrational states are indicated schematically by the light horizontal lines; for the  $H_2^+$  ion there are actually 19 bound vibrational states. In the presence of an electric field this potential remains unperturbed in lowest order for heteronuclear molecules and homonuclear systems in even charge states.



MU-20334

Fig. 3. The nuclear potential for a homonuclear ion in an odd charge state in the presence of an electric field. The vibrational states are indicated schematically by the light horizontal lines. The asymptotic potential for the lower electronic state falls off as

$$-\frac{1}{2} \epsilon \mathcal{E} |z_n|.$$



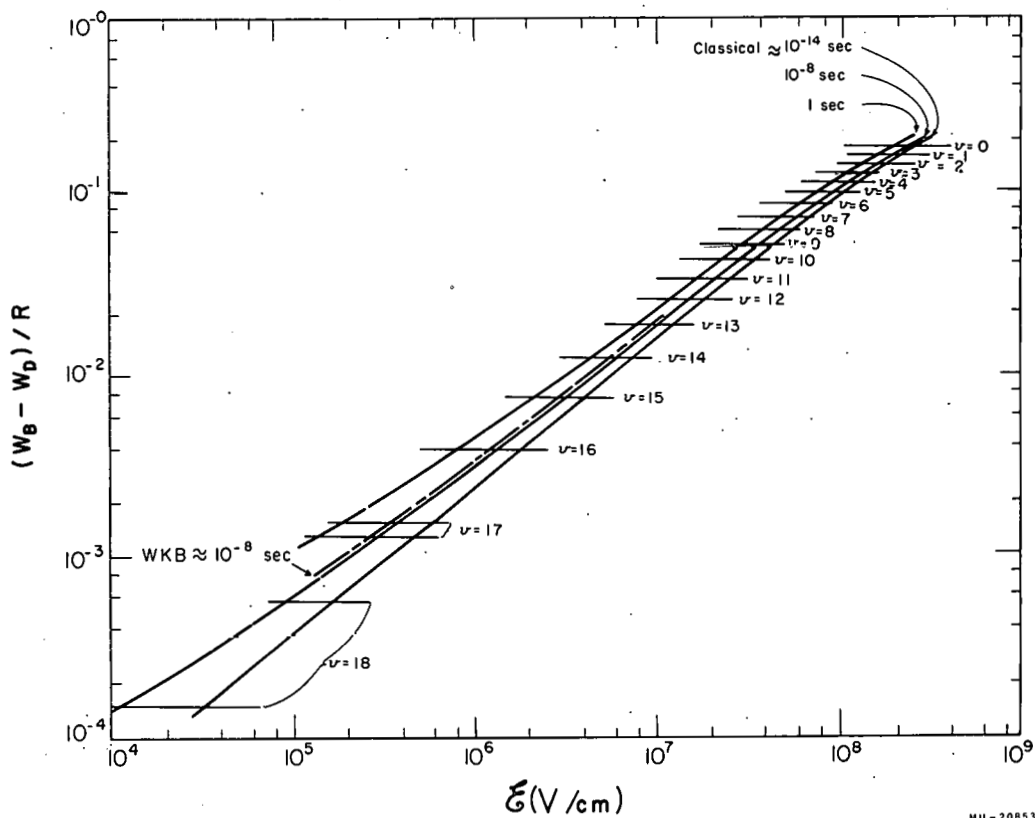
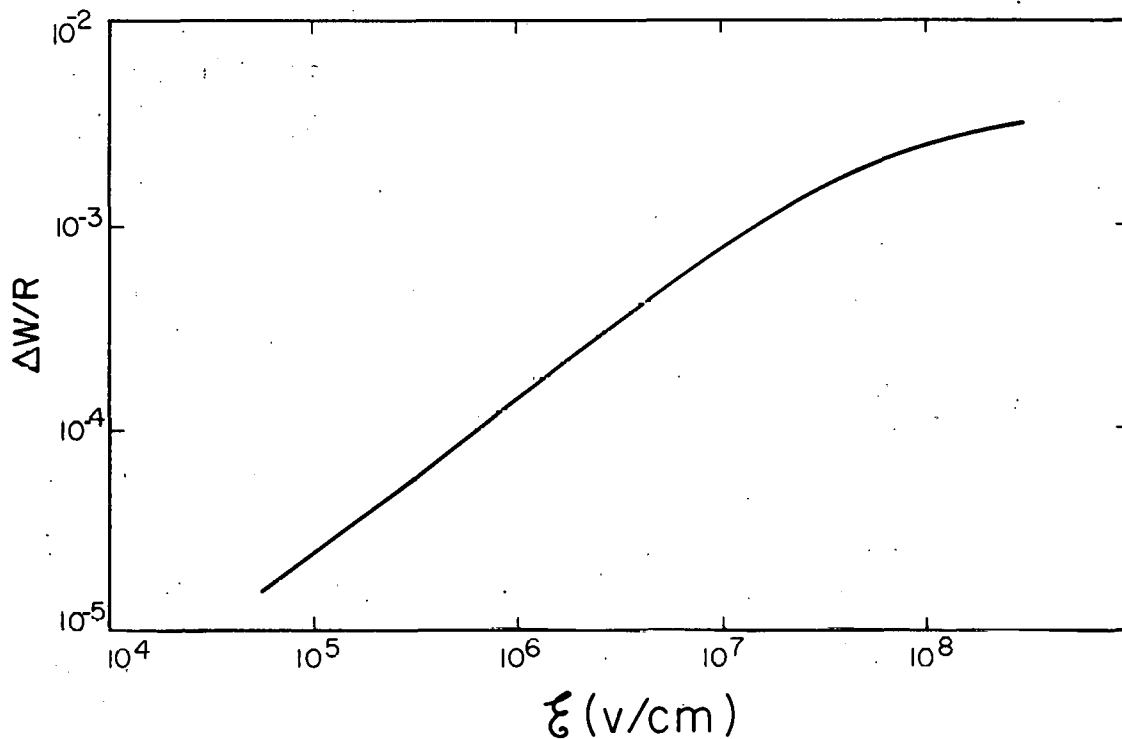
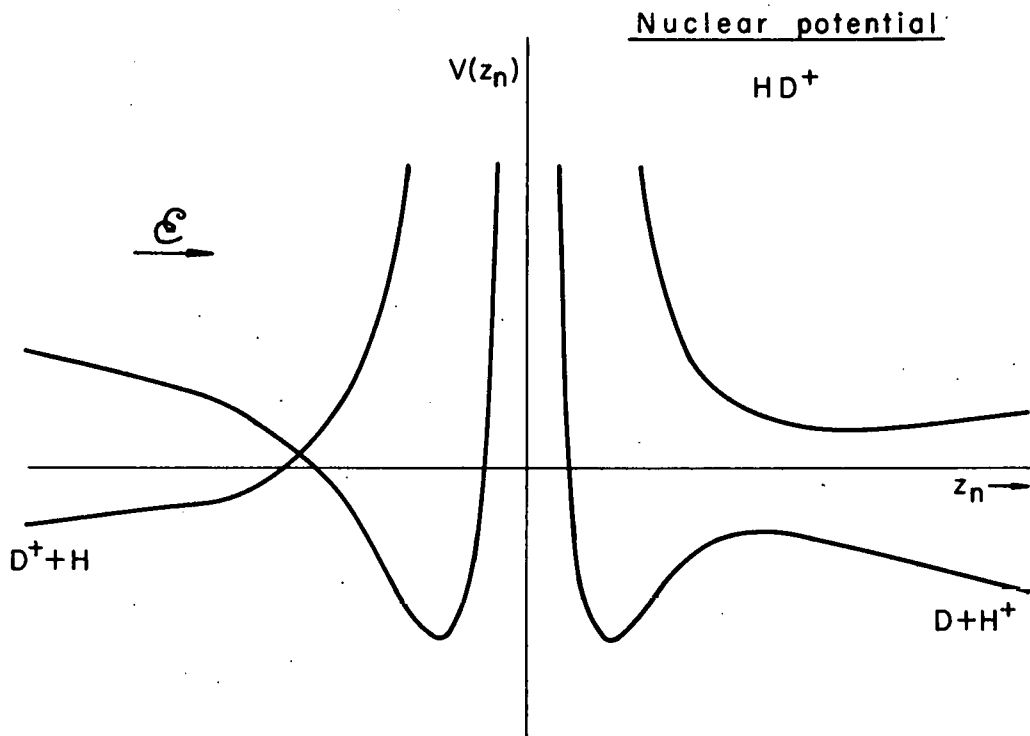


Fig. 4. Binding energy measured from the unperturbed dissociation limit versus electric field for the various vibrational states of the  $H_2^+$  ion and for  $J=0$ . The intersection of the horizontal lines with the curve marked "classical" determines the electric field necessary to dissociate the ion 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.



MU-20854

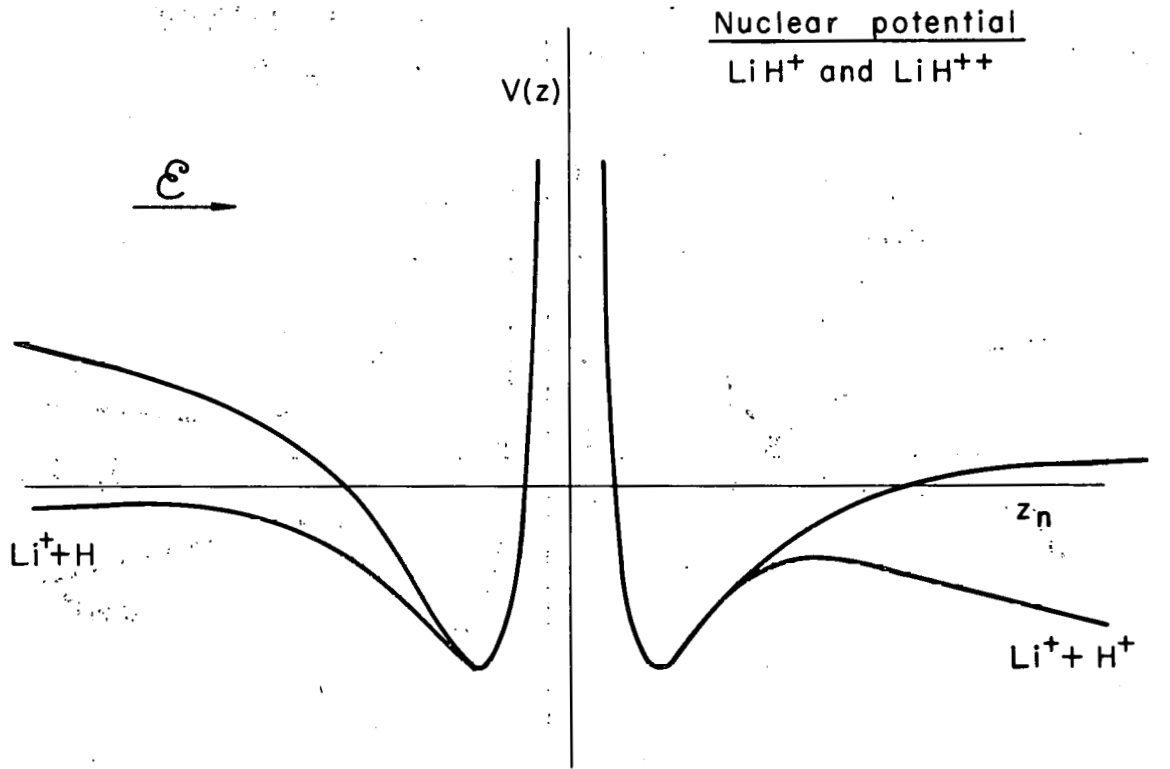
Fig. 5. First-order perturbation versus electric field for the various vibrational states of the  $H_2^+$  ion. The perturbation for each vibrational level has been calculated using for the electric field the value given by the curve labeled "classical" in Fig. 4.



MU - 20335

Fig. 6. The nuclear potential for  $HD^+$  in the presence of an electric field. The asymptotic potential for the lower electronic state varies as

$$-\frac{2}{3} \epsilon_0^2 z_n^3$$



MU-20336

Fig. 7. A comparison of the asymptotic nuclear potentials for the LiH<sup>+</sup> and LiH<sup>++</sup> ions. The asymptotic potential for the singly ionized ion varies as,

$$+\frac{1}{8} \epsilon \mathcal{E} z_n,$$

$$-\frac{3}{4} \epsilon \mathcal{E} z_n.$$

This diagram is meant to be indicative only, it is not known whether the doubly ionized ion has a stable ground state.

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