

Here we may infer that it is possible that such a minimum in the free-positron annihilation rate also exists in nitrogen. If such a minimum does exist, it is reasonable to assume that it exists even at low positron energy corresponding to the minimum in the $\lambda(t)$ plot (Figs. 10 and 11). Since the minimum in the $\lambda(t)$ plot occurs within 2 nsec amagat (?) of $t = 0$, that is, the probable time for slowing down to 0.29 eV the minimum in the free-positron annihilation rate should exist at an energy about or higher than 0.29 eV. A reasonable guess would be about 0.5 eV. The free annihilation rate at the minimum is

estimated from the $\lambda(t)$ values shown in Figs. 10 and 11 to be about $4.5 \text{ nsec}^{-1} \text{ amagat}^{-1}$, which is equivalent to $Z_{\text{eff}} = 23$.

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Stark and Zeeman Effects on the Protonic Structure of Molecules*

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The effect of a homogeneous electric field on the protonic coordinates of neutral hydrides is shown to be identical to the effect on the electronic coordinates. For ionized hydrides, the effects on the protonic coordinates are shown to be proportional to $(1 - Nm_p/M)$ where m_p and M are the protonic and total mass, respectively, and N is the degree of ionization. A homogeneous magnetic field affects the protonic coordinates through terms proportional to $\mathcal{H}^2 m_p/M$ and $N_e \mathcal{H}^2 m_p^2/M^2$, where \mathcal{H} is the strength of the field and N_e is the number of electrons in the molecule. The terms of first order in \mathcal{H} are found to be negligible for the protonic coordinates. The effects of both the electric and magnetic fields on the motion of the center of mass are also given. We show that in the presence of a homogeneous magnetic field in the z direction, the center of mass of neutral atoms or molecules will vibrate in the xy plane with a frequency of $\omega = (N_e q_e^2 \mathcal{H}^2 / 4Mm_e c^2)^{1/2}$, where c is the velocity of light.

In several papers we have established theoretically the existence of a protonic structure in molecules completely analogous to the electronic structure.¹ The field free Hamiltonian which we used was, in hartrees,

$$H = \sum_i \left(\frac{-1}{2m_i} \nabla_i^2 + \sum_{j>i} \frac{q_i q_j}{r_{ij}} \right),$$

where the sums over i and j run over all the nuclei and electrons of the molecule, m_i and q_i are the

mass and charge of the i th particle, and r_{ij} is the distance between particles i and j .

In this paper, we will add to the field free Hamiltonian external homogeneous electric and magnetic fields.

Our wave functions are in center-of-mass coordinates; therefore, we must transform the operator

$$H' = -F(q_a z_a + \sum_i q_i z_i) \quad (1)$$

to those coordinates defined by

$$\vec{R}_i = \vec{r}_i - \vec{r}_a$$

and

$$\vec{R} = (m_a \vec{r}_a + \sum_i m_i \vec{r}_i) / M,$$

where \vec{r}_i is the position vector of the i th particle, \vec{r}_a is the position vector of the particle at the origin of the relative coordinate system, and $M = m_a + \sum_i m_i$, where the m 's represent the masses of the particles. Substitution of $Z_i + z_a$ for z_i in Eq. (1) leads to

$$H' = -F(q_a z_a + z_a \sum_i q_i + \sum_i q_i Z_i).$$

For neutral molecules, $\sum_i q_i = -q_a$, and

$$H' = -F \sum_i q_i Z_i = -F(\sum_A Z_A - \sum_I Z_I), \quad (2)$$

where Z_A and Z_I are the protonic and electronic coordinates, respectively. In order to treat ions let $q_a = N_e - N_p + N$, where N_e is the number of electrons, N_p is the number of protons, and N is the number of electrons or protons ionized. Note that N is negative when it refers to the number of protons ionized and positive when it refers to the number of electrons ionized. Our operator becomes

$$H' = -F(Nz_a + \sum_i q_i Z_i).$$

In the c. m. coordinates we find

$$z_a = Z - \sum_i (m_i / M) Z_i.$$

Therefore,

$$\begin{aligned} H' &= -F[NZ + \sum_i (1 - Nm_i/q_i M) q_i Z_i] \\ &\approx -F[NZ - \sum_I Z_I + \sum_A (1 - Nm_A/M) Z_A], \quad (3) \end{aligned}$$

since the electronic mass is much smaller than M . The field in this case affects the motion of the center of mass. Note that for $N=0$ Eq. (3) becomes Eq. (2). Also note that the effect on the protonic coordinates increases when protons are ionized and decreases when electrons are ionized.

The Hamiltonian of a molecule in a homogeneous magnetic field is

$$\begin{aligned} H &= \sum_j \left[\frac{1}{2m_j} \left(\frac{\hbar}{i} \nabla_j - \frac{q_j A_j}{c} \right)^2 + \frac{q_j}{m_j c} \vec{\mathcal{C}} \cdot \mathbf{s}_j \right] + V \\ &= \sum_j \left(\frac{-\hbar^2}{2m_j} \nabla^2 + \frac{iq_j \hbar}{m_j c} (A_j \cdot \nabla_j) \right. \\ &\quad \left. + \frac{q_j^2 \hbar}{2m_j c} A_j^2 + \frac{q_j}{m_j c} \vec{\mathcal{C}} \cdot \mathbf{s}_j \right) + V. \end{aligned}$$

Let $A_x = -\frac{1}{2} \mathcal{C} y$, $A_y = \frac{1}{2} \mathcal{C} x$, and $A_z = 0$ so that we represent a homogeneous magnetic field in the z direction. The Hamiltonian becomes

$$H = H_0 + H',$$

where

$$H_0 = \sum_j (-\hbar^2 / 2m_j) \nabla_j^2 + V$$

and

$$\begin{aligned} H' &= \sum_j \left[\frac{iq_j \hbar}{m_j c} \left(x \frac{\partial}{\partial y} - y \frac{\partial}{\partial x} \right)_j \right. \\ &\quad \left. + \frac{q_j^2}{8m_j c^2} \vec{\mathcal{C}}^2 (x^2 + y^2)_j + \frac{q_j \hbar}{m_j c} \vec{\mathcal{C}} \cdot \mathbf{s}_j \right]. \end{aligned}$$

We will now transform H' to c. m. coordinates starting with $\sum_j q_j^2 x_j^2 / m_j$:

$$x_j^2 = (X_j + x_a)^2 = X_j^2 + 2x_a X_j + x_a^2,$$

but

$$x_a = X - \sum_k (m_k / M) X_k;$$

therefore,

$$x_j^2 = X_j^2 + 2[X - \sum_k \frac{m_k}{M} X_k] X_j + x_a^2$$

and

$$\begin{aligned} \frac{q_a^2}{m_a} x_a^2 + \sum_j \frac{q_j^2}{m_j} x_j^2 &= \sum_j \frac{q_j^2}{m_j} \left[X_j^2 + 2 \left(X - \sum_k \frac{m_k}{M} X_k \right) X_j \right] \\ &\quad + \left(\frac{q_a^2}{m_a} + \sum_j \frac{q_j^2}{m_j} \right) \left(X^2 - 2X \sum_k \frac{m_k}{M} X_k \right. \\ &\quad \left. + \sum_k \sum_l \frac{m_k m_l}{M^2} X_k X_l \right), \end{aligned}$$

where q_a and m_a are the charge and mass of the nucleus at the origin. We can neglect all terms involving m_e/M where m_e is the mass of the electron. Also $q_a^2/m_a < q_p^2/m_p \ll q_e^2/m_e$, where q_p and m_p are the charge and mass of the proton, respectively, and q_e is the electronic charge. Therefore, our expression reduces to

$$\begin{aligned} &\approx (q_e^2/m_e) \left\{ \sum_I [X_I^2 + 2XX_I - \sum_A (m_p/M) X_A X_I] \right. \\ &\quad \left. + N_e [X^2 - 2X \sum_A (m_p/M) X_A + \sum_A \sum_B (m_p^2/M^2) X_A X_B] \right\}, \end{aligned}$$

where the index I refers to electrons and the index A refers to protons. We will assume that the interaction of the c. m. motion with the internal coordinates is small. It should be kept in mind, however, that we have not justified this assumption. The assumption leads to

$$\begin{aligned} \sum_j (q_j^2/m_j) (x_j^2 + y_j^2) &\approx \frac{q_e^2}{m_e} \left\{ \sum_I [(X_I^2 + Y_I^2) \right. \\ &\quad \left. - (m_p/M) (X_I \sum_A X_A + Y_I \sum_A Y_A)] \right\} \end{aligned}$$

TABLE I. Resonance frequencies and wavelengths of the noble gases at 10 000 G.

	He	Ne	Ar	Kr	Xe
$\omega(\times 10^{-6})$	1456.02	1449.86	1382.65	1350.06	1320.95
$\lambda(\text{cm})$	20.5899	20.6772	21.6825	22.2059	22.6952

$$+ N_e [X^2 + Y^2 + (m_p^2/M^2) \sum_A \sum_B (X_A X_B + Y_A Y_B)] .$$

In the second period, $N_e m_p^2/M^2$ ranges from $\frac{1}{16}$ for LiH to $\frac{1}{10}$ for HF. For the hydrogen molecule it is about $\frac{1}{2}$. The m_p/M term is $\frac{1}{8}$ for LiH, $\frac{1}{10}$ for HF, and $\frac{1}{2}$ for H₂. So we see that the effect on the protonic coordinates decreases rapidly as M increases. The effect on the c. m. coordinates increases as the number of electrons increase.

We will now transform the angular momentum operator:

$$\begin{aligned} \sum_j \frac{q_j x_j}{m_j} \frac{\partial}{\partial y_j} &= \sum_j \left[\left(1 - \frac{m_j}{M} \right) X_j + X - \sum_{k \neq j} \frac{m_k}{M} X_k \right] \\ &\times \left(\frac{q_j}{m_j} \frac{\partial}{\partial y_j} + \frac{q_j}{M} \frac{\partial}{\partial Y} \right) \frac{q_a x_a}{m_a} \frac{\partial}{\partial y_a} \\ &= \left(X - \sum_j \frac{m_j}{M} X_j \right) \left(\frac{q_a}{M} \frac{\partial}{\partial Y} - \sum_j \frac{q_a}{m_a} \frac{\partial}{\partial Y_j} \right) . \end{aligned}$$

When we add the above two equations and neglect all terms of order $1/m_a$ or smaller which involve

the internal coordinates, we get

$$\begin{aligned} &\approx \frac{q_e}{m_e} \sum_I \left(X_I + X - \frac{m_p}{M} \sum_A X_A \right) \frac{\partial}{\partial Y_I} \\ &+ \frac{q_p}{m_p} \sum_A \left(X_A + X \right) \frac{\partial}{\partial Y_A} + \frac{1}{M} \left(q_a + \sum_j q_j \right) X \frac{\partial}{\partial Y} . \end{aligned}$$

We see that the effect on the protonic coordinates is about 2000 times less than on the electronic coordinates. We found this result also in the magnetic dipole operator when we investigated the selection rules for adsorption of light.² When we neglect terms of order $1/m_p$ or less in the internal coordinates and assume that the interaction between the c. m. coordinates and internal coordinates is small, we get for the angular momentum operator

$$\frac{q_e}{m_e} \sum_I \left(X_I \frac{\partial}{\partial Y_I} - Y_I \frac{\partial}{\partial X_I} \right) + \frac{N q_e}{M} \left(X \frac{\partial}{\partial Y} - Y \frac{\partial}{\partial X} \right) ,$$

where N is the number of protons or electrons ionized.

The final term in H' is important only for the electrons. Thus when we gather everything together, we get

$$\begin{aligned} H' &\approx \sum_I \left[\frac{i q_e \hbar \mathcal{K}}{m_e c} \left(X_I \frac{\partial}{\partial Y_I} - Y_I \frac{\partial}{\partial X_I} \right) + \frac{q_e^2 \mathcal{K}^2}{8 m_e c^2} \left((X_I^2 + Y_I^2) - \frac{m_p}{M} (X_I \sum X_A + Y_I \sum Y_A) \right) + \frac{q_e \hbar}{m_e c} \mathcal{K} \cdot s_I \right] \\ &+ \frac{N_e q_e^2 m_p^2 \mathcal{K}^2}{8 m_e M^2 c^2} \sum_A \sum_B (X_A X_B + Y_A Y_B) + \frac{i N q_e \hbar \mathcal{K}}{M c} \left(X \frac{\partial}{\partial Y} - Y \frac{\partial}{\partial X} \right) + \frac{N_e q_e^2 \mathcal{K}^2}{8 m_e c^2} (X^2 + Y^2) . \end{aligned}$$

For neutral atoms or molecules $N=0$, and the Hamiltonian for the motion of the center of mass becomes that of a harmonic oscillator with a frequency

$$\omega = K(N_e/M)^{1/2} ,$$

where if $\mathcal{K} = 10\,000$ G,

$$K = \left(\frac{q_e^2 \mathcal{K}^2}{4 m_e c^2} \right)^{1/2} = 2.65418 \times 10^{-3} \text{ g}^{1/2} \text{ sec}^{-1} .$$

The energy levels are $E = \frac{1}{2}(2n+1)\hbar\omega$. For example, the resonance frequencies of the noble gases are given in Table I. We expect in the near future to report the results of experiments which we are doing to test the above result.

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