

specified, would provide a convenient starting point for calculations.

Final-state configurations in transitions of type (1) correspond to two different types of M holes. The first configuration contains an electron hole in both the K and the M_I shells, and the second contains a hole in both the K and the M_{II} or M_{III} shells. Transitions which result in these two final-state configurations should give rise to two resonance absorption structures appreciably different in energy position in the spectrum. The energy difference is given roughly by the $M_{II,III}$ to M_I separation in a hydrogenic atom, with the $M_{II,III}$ structure appearing at the lower energy. Theoretical evaluation of the energy separation $P_{KM} - P_K$ has not been made but, if P_{KM} refers to missing K and $M_{II,III}$ electrons, this energy separation should correspond roughly with the energy of the $M_{II,III}$ state in singly ionized potassium (which closely approximates an argon atom with a missing K electron). A first approximation to the relative intensity to be expected in the $KM_{II,III}$ and KM_I resonance structures is given by the ratio of the number of electrons in each shell, namely $(6/2) = 3$.

Since only one new resonance structure was, in fact,

observed in the range 0 to 50 eV beyond the position of P_K , it seems plausible to assign this new structure, because of its energy position, to processes involving $M_{II,III}$ electrons. With this assignment, the absence of the KM_I resonance structure is perhaps reasonable on the basis of the intensity argument above—the KM_I structure would be barely above the experimental noise.

To recapitulate, a new structure has been observed in the K absorption spectrum of argon. This new structure is tentatively interpreted as arising from the simultaneous excitation of two electrons by an absorption of a single photon. The observations are particularly interesting since the physical system dealt with is a very simple experimental and theoretical case, namely, a monoatomic, noninteracting atom.

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Proton Scattering by Molecules. I. The Two-State Oxygen Case and the Multistate Case*

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The inelastic scattering of protons by oxygen molecules is treated for the collision situation resulting in the excitation of the upper state of the Schumann-Runge system. The incident proton energy ranges from 1 to 50 keV. The total cross sections and the growth coefficient phases for this scattering are computed using the two-state impact-parameter treatment. The distortion of the molecular charge cloud by the incident proton is taken into account in the phase calculation. A method for multistate impact parameter treatment of the inelastic collision is developed, and the equations therefor are derived.

I. INTRODUCTION

HERE we consider the inelastic collision of protons with oxygen molecules resulting in the excitation of the Schumann-Runge system of oxygen. The proton energies range from 1 to 50 keV. The impact parameter treatment will be applied. This treatment was effectively introduced by Gurnee and Magee¹ in their study of charge transfer scattering. It has been discussed in connection with certain inelastic and charge transfer

hydrogen collisions by Bates² and somewhat improved upon by McCarroll.^{3,4} The very slight differences between their treatment and ours seem to warrant a brief derivation.

In Sec. II the two-state impact-parameter formulation is discussed. In Sec. III the inelastic-scattering cross section for protons on oxygen molecules with the excitation of the Schumann-Runge system is calculated. In Sec. IV the phase of the initial-state growth coefficient is computed. For this computation

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¹ E. F. Gurnee and J. L. Magee. *J. Chem. Phys.* **26**, 1237 (1957).

² D. R. Bates. *Proc. Roy. Soc. (London)* **A245**, 299 (1958).

³ R. McCarroll. *Proc. Roy. Soc. (London)* **A246**, 547 (1961).

⁴ *Atomic and Molecular Processes*, edited by D. R. Bates (Academic Press Inc., New York, 1962).

the effects of molecular orbital polarization by the proton are included. In Sec. V a general formulation of the impact parameter treatment for the multistate case is detailed.

II. THE TWO-STATE IMPACT PARAMETER FORMULATION

At $t = -\infty$ the proton of initial momentum k is at infinite separation from the target molecule which is in its ground state. At time $t = +\infty$ the molecular state and the proton momentum have been changed by collision. We represent the wave functions for the initial- and final-system state by the exact solutions of the Schrödinger equation for infinite separation:

$$\psi_i = \varphi_i(\mathbf{r}_m) \frac{1}{r} \exp[-i\mathbf{k} \cdot \mathbf{r} - iE_\tau t], \quad (1a)$$

$$\psi_f = \varphi_f(\mathbf{r}_m) \frac{1}{r} \exp[i\mathbf{k}' \cdot \mathbf{r} - iE_\tau' t]. \quad (1b)$$

The φ_k refer to the molecular wave functions while the remainder of the product refers to the protons. The proton coordinates are referred to the stationary molecule. The proton portions of the system wave function have no direct effect on this calculation; however, they do lead to the reduction of the result to the Born approximation for high v or low H_{if}' , as will be shown. From Eqs. (1) we may obtain the following approximation for the system equations:

$$\Psi(\mathbf{r}, t) = a_i(t)\psi_i \exp(-iE_i t) + b_f(t)\psi_f \exp(-iE_f t). \quad (2)$$

The a_i and b_f are the state growth coefficients. When we substitute Eq. (2) into the Schrödinger equation, it is apparent that, since Eqs. (1) are exact solutions to the infinite equation, all terms in the Schrödinger equation will drop out save those involving the potential of interaction and the rates of change of the state growth coefficients.

In order to facilitate future manipulations, we now absorb the exponentials involving $\mathbf{k} \cdot \mathbf{r}$ into the state growth coefficients. The Schrödinger equation is multiplied through on the left, first by

$$\varphi_i^*(\mathbf{r}_m) \exp[iE_i t] r \exp[iE_\tau t],$$

and then by

$$\varphi_f^*(\mathbf{r}_m) \exp[iE_f t] r \exp[iE_\tau' t].$$

After integration over the proper space coordinates, the resulting equations may be added and the one equation thus obtained dealt with in the manner of Gurnee and Magee in order to obtain

$$A_i + B_f = e^{-iQ}, \quad Q = \int_{-\infty}^{\infty} \frac{1}{v} (H_{ii}' + H_{if}') dx. \quad (3)$$

The normality condition is

$$(\Psi^*, \Psi) = a_i^* a_i + b_f^* b_f = 1. \quad (4)$$

We now make the following assumptions as to the state growth coefficients:

$$A_i = \rho e^{i\omega} e^{-i\mathbf{k} \cdot \mathbf{r}} \quad B_f = \rho' e^{i\omega'} e^{i\mathbf{k}' \cdot \mathbf{r}}, \quad (5)$$

and Eqs. (4) and (5) combine in an amplitude relationship. From the Schrödinger equation the following equations may be obtained:

$$\rho e^{i\omega} H_{ii}' + (1 - \rho^2)^{1/2} + e^{i\omega'} H_{if}' \exp[i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}] = -\dot{\omega} \rho e^{i\omega} + i\dot{\rho} e^{i\omega}, \quad (6a)$$

$$\rho e^{i\omega} H_{if}' \exp[-i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}] + i(1 - \rho^2)^{1/2} e^{i\omega'} H_{ff}' = -\dot{\omega}' (1 - \rho^2)^{1/2} e^{i\omega'} - [i/(1 - \rho^2)^{1/2}] e^{i\omega'}. \quad (6b)$$

From Eqs. (6) the relationship between ω and ω' is established. This in turn allows us to arrive at the following expression for the initial amplitude.

$$\int_1^{\rho^2} \frac{d\rho}{(1 - \rho^2)^{1/2}} = \int_{-\infty}^x \frac{1}{v} H_{if}' \exp[i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}] dx, \quad (7)$$

where the impact parameter relationship between time and distance along the rectilinear collision path has been assumed. From this equation the following expression for the final state growth coefficient results:

$$|b_f(\infty)|^2 = |(1 - \rho_\infty^2)^{1/2}|^2 = \left| \sin \left\{ \int_{-\infty}^{+\infty} \frac{1}{v} H_{if}' \exp[i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}] dx \right\} \right|^2. \quad (8)$$

From Eq. (8) we write

$$\begin{aligned} b_f &= \sin \left\{ \int \frac{1}{v} H_{if}' \exp[i(\mathbf{k} + \mathbf{k}') \cdot \mathbf{r}] dx \right\} \\ &= \sin \left\{ \frac{1}{v} \int H_{if}' \exp \left[\frac{i}{v} (E_f - E_i) x \right] dx \right\} \\ &= \frac{1}{v} \int H_{if}' \exp \left[\frac{i}{v} (E_f - E_i) x \right] dx \\ &\quad - \frac{1}{3! v} \left\{ \int H_{if}' \exp \left[\frac{i}{v} (E_f - E_i) x \right] dx \right\}^3 + \dots \end{aligned}$$

For high velocities or weak interactions this expression reduces to the first term which Arthurs⁵ has shown is equivalent to the Born approximation.

We recall that the probability for transition and, hence, for the inelastic scattering under consideration here is the square of this state growth coefficient after infinite time. In order to obtain the cross section we simply average over impact parameter with the following results:

$$\sigma = 2\pi \int_0^\infty |b_f(\infty)|^2 \rho d\rho. \quad (9)$$

⁵ A. M. Arthurs, Proc. Cambridge Phil. Soc. 57, 904 (1961).

III. THE TWO-STATE IMPACT PARAMETER CROSS SECTION FOR THE PROTON OXYGEN CASE

The interaction Hamiltonian is

$$H' = -\frac{8}{r_a} - \frac{8}{r_b} + \sum_{i=1}^{16} \frac{1}{r_i}. \quad (10)$$

The matrix element of Eq. (10) over the lower ${}^3\Sigma_g^-$ and upper ${}^3\Sigma_u^-$ states of oxygen is to be evaluated. We use the single determinant wave functions for these states as developed by Kotani *et al.*⁶ The only difference in the two functions is that a π_u^- orbital in the ground state is replaced by a π_g^- orbital in the upper state. This means that H_{if}' will reduce to the integral of H' over these two orbitals since the orbitals are orthogonal and since H' is a one-particle operator insofar as the molecule is concerned. Hence,

$$H_{if}' = \int \frac{1\pi_u 1\pi_g}{r_{ie}} d\tau_i. \quad (11)$$

This may be evaluated directly using the orbitals

$$1\pi_u = 0.7631 \left(\frac{\delta^5}{\pi}\right)^{1/2} \{r_a e^{-\delta r_a} \sin\vartheta_a + r_b e^{-\delta r_b} \sin\vartheta_b\} e^{i\varphi},$$

$$1\pi_g = 0.6619 \left(\frac{\delta^5}{\pi}\right)^{1/2} \{r_a e^{-\delta r_a} \sin\vartheta_a - r_b e^{-\delta r_b} \sin\vartheta_b\} e^{i\varphi},$$

and $r_{ie}^{-1} \doteq r_{>}^{-1}$ with the result

$$H_{if}' = C \left\{ \left[\frac{R^2}{(2\delta)^2} + \frac{6R}{(2\delta)^3} + \frac{18}{(2\delta)^4} + \frac{24}{(2\delta)^5 R} \right] e^{-2\delta R} - \left[\frac{(R+d)^2}{(2\delta)^2} + \frac{6(R+d)}{(2\delta)^3} + \frac{18}{(2\delta)^4} + \frac{24}{(2\delta)^5 (R+d)} \right] e^{-2\delta R} e^{-2\delta d} \right\} - \frac{24C}{(2\delta)^5 R} + \frac{24C}{(2\delta)^5 (R+d)}. \quad (12)$$

in Eq. (12), d is the internuclear separation, 2.282; δ is the effective nuclear charge, 2.275; and C is a constant of magnitude 82.0816.

In arriving at Eq. (12) we have taken the proton path as restricted to the molecular symmetry axis. If the proton path is taken as lying anywhere in the plane perpendicular to the molecular symmetry axis and containing the molecular center of symmetry, $1\pi_g$ and, hence, H_{if}' will be zero. We, therefore, restrict the proton path to the symmetry axis and argue that the

⁶ M. Kotani, Y. Mizuno, K. Kayama, and E. Ishiguro, *J. Phys. Soc. (Japan)* **12**, 707 (1957).

path will approximate a number of probable trajectories.

Equation (12) has been plotted and fitted by the following:

$$H_{if}' = -\frac{1.00861}{R} + \frac{1.00816}{R+d}. \quad (13)$$

Equation (13) is used in the evaluation of Eq. (8) after the latter equation has been somewhat simplified. First the proton velocity is taken as a constant v , for $-\infty \leq x < 0$. At this point the velocity changes instantaneously to its final value v' . The inner product in the exponential then becomes

$$\mathbf{k} \cdot \mathbf{r} = -kr \cos(\pi - \vartheta) = kr(x/r). \quad (14)$$

In Eq. (14) x is the proton coordinate along its assumed rectilinear path while r and ϑ are the proton coordinates relative to the near nucleus in the molecule. The curly-bracketed expression in Eq. (8) becomes

$$\frac{1}{v} \int_{-\infty}^0 H_{if}' \exp[-i(k-k')x] dx + \frac{1}{v'} \int_0^{\infty} H_{if}' \exp[-if(k-k')x] dx. \quad (15)$$

Equation (15) may be rewritten as

$$\left(\frac{1}{v} + \frac{1}{v'}\right) \int_0^{\infty} H_{if}' \cos[(k-k')x] dx + i \left(\frac{1}{v} - \frac{1}{v'}\right) \int_0^{\infty} H_{if}' \sin[(k-k')x] dx.$$

The right side of Eq. (8) now becomes

$$\sin^2 \left\{ \left(\frac{1}{v} + \frac{1}{v'}\right) \int_0^{\infty} H_{if}' \cos[(k-k')x] dx \right\} + \sinh^2 \left\{ \left(\frac{1}{v} - \frac{1}{v'}\right) \int_0^{\infty} H_{if}' \sin[(k-k')x] dx \right\}. \quad (16)$$

The second term in Eq. (16) gains importance at energies below one thousand electron volts. At 1 keV for our case, it is about two orders of magnitude smaller than the first term for all values of the impact parameter. We therefore drop the term.

For 1000 V and above,

$$\cos[(k-k')x] \doteq 1.$$

Thus, Eq. (8) now has the form

$$|b_f(\infty)|^2 = \sin^2 \left[\left(\frac{1}{v} + \frac{1}{v'}\right) \int_0^{\infty} H_{if}' dx \right], \quad (17)$$

which is what would have resulted from an assumption of post and prior momentum equality in Eq. (16).

This expression has been evaluated on a desk computer for a sufficient number of impact parameters to

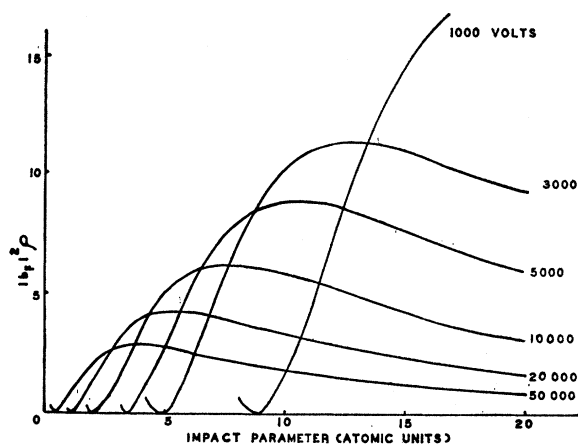


FIG. 1. The behavior of the cross-section integrand with impact parameter for the various proton energies.

allow evaluation of Eq. (9) for Schumann-Runge excitation and for values of the proton translational energy ranging from 1 to 50 keV. The method of evaluation we now describe.

If the behavior of $|b_f|^2$ is traced inward from large ρ , we find that it is a monotonically increasing function until a point a few units from the nucleus is reached. At this point the function passes through a maximum and then oscillates more and more rapidly with lesser separation. The integration inward is numerical to the first minimum and will be discussed in a moment. From the first minimum, however, we take $|b_f|^2 \cong \frac{1}{2}$ so that the integral has a value $\frac{1}{4}\rho_{\min}$ for this inner portion.

If the infinite upper limit for the integral in Eqs. (8) and (16) is retained, the form of the interaction will lead to a divergence. This is a formal difficulty at worst since the upper limit on the interaction will *not* be infinite; it will be determined by the shielding effect of the other particles. We choose the upper limit as the Debye radius. For the present, however, we may not specifically evaluate this since we are working with no particular temperature and density. We chose the limit as fifty units.

In Fig. 1 we illustrate the behavior of the cross-section integrand for various energies as a function of impact parameter. The total cross sections which result are given for this energy range in Fig. 2.

IV. THE INITIAL-STATE GROWTH COEFFICIENT PHASE

We may obtain an equation for the phase of the initial state growth coefficient from Eq. (6a). When a rectilinear classical path is again assumed, this equation leads immediately to

$$\omega_p = - \int_{-\infty}^{+\infty} \frac{1}{v} H_{ii}' dx \cong - \frac{1}{v} \int_{-\infty}^{+\infty} H_{ii}' dx. \quad (18)$$

The matrix element of the interaction operator is

given by

$$H_{ii}' = \int H' |\Psi(^2\Sigma_g^-)|^2 d\tau. \quad (19a)$$

The $\Psi(^2\Sigma_g^-)$ is again taken as a single determinant with the result

$$H_{ii}' = \sum_i \int H' |\chi_i|^2 d\tau, \quad (19b)$$

where the χ_i are the molecular orbitals.

In evaluating Eq. (11) we have used molecular orbitals which were undistorted by the presence of the proton. This has been done because our method of orbital distortion⁷ requires a basis set of more than one orbital of the same symmetry, and such sets are simply not available for the π orbitals. The sigma orbitals also enter the evaluation of Eq. (19b), and they will be distorted. We have recently shown⁸ that the distortion of the sigma orbitals is evidently much more important than the distortion of the π orbitals.

The following form for the distorted orbitals has been developed⁷:

$$\chi_i = [1 + a r_i \cos \theta_i] \chi_i^{(0)}, \quad (20a)$$

$$a_i = \frac{(\chi_i^{(0)} | H' | \chi_j^{(0)})}{(\chi_j^{(0)} | r_i \cos \theta_i | \chi_i^{(0)}) (E_i^0 - E_j^0)}. \quad (20b)$$

In Eqs. (20) H' is the interaction operation, $\chi_i^{(0)}$ is an undistorted orbital, and E_i is the undistorted energy corresponding to the i th orbital. The distortion coefficients a_i have been computed for the oxygen orbitals for the proton interaction, and these orbitals used in the evaluation of Eq. (19b). Again the on-axis proton path was assumed. The result is

$$H_{ii}' = V^{(0)} + d \{ [0.86842 a_{2\sigma_g} + 0.13084 a_{3\sigma_g} + 0.88962 a_{2\sigma_u}] V_{2s}^{(0)} + [0.13076 a_{2\sigma_g} + 0.86923 a_{3\sigma_g} + 0.11040 a_{2\sigma_u}] V_{2p}^{(0)} \}, \quad (21a)$$

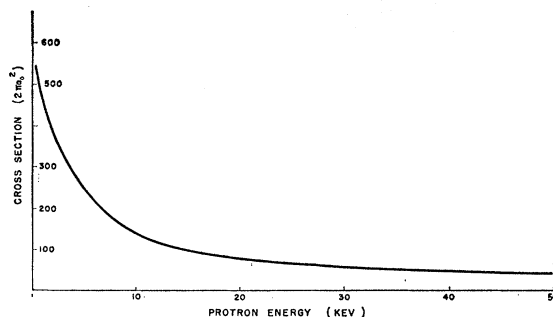


FIG. 2. The cross section for the inelastic collision of a proton with an oxygen molecule resulting in the excitation of the Schumann-Runge system.

⁷ R. G. Breene, Jr., J. Quart. Spectr. Radiative Transfer **2**, 225 (1962).

⁸ R. G. Breene, Jr., J. Quart. Spectr. Radiative Transfer (to be published).

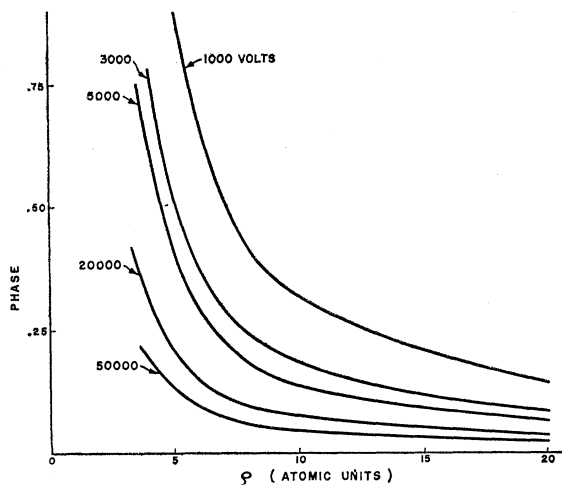


FIG. 3. The state growth coefficient phase as a function of impact parameter and proton energy.

$$V_{2s}^{(0)} = (19.165R^2 + 9.184R + 4.465 + 1/R)e^{-5.718R} + 1/R, \quad (21b)$$

$$V_{2p}^{(0)} = (3.523R^2 + 4.816R + 3.292 + 1/R)e^{-4.389R} + 1/R, \quad (21c)$$

$$V^{(0)} = (15.322 + 2/R)e^{-15.322R} + (38.330R^2 + 18.368R + 8.930 + 2/R)e^{-5.718R} + (14.092R^2 + 19.264R + 13.168 + 4/R)e^{-4.389R}. \quad (21d)$$

In Eq. (21a), d is the internuclear separation in the molecule. Although the wave functions of Kotani *et al.* were used for the distortion coefficient calculation, our own atomic wave functions⁹ were used for the evaluation of the $V_i^{(0)}$.

Equation (21a) has been evaluated numerically. A reasonable fit to the resulting curve is provided by the following much simplified function:

$$H_{ii}' = -e^{-0.1209R} (3.14012/R^2 - 0.46214/R + 0.030832), \quad (22)$$

where

$$R = (x^2 + \rho^2)^{1/2}.$$

Equation (18) may now be evaluated for the various v as a function of ρ . A few examples are given in Fig. 3.

V. THE IMPACT PARAMETER TREATMENT FOR THE MULTISTATE CASE

Now let us consider the molecule as possessing a large number of bound states. First, we take the following expression as the wave function for the proton-molecule system:

$$\Psi = \sum c_i(t) \varphi_i(\mathbf{r}_m) \frac{1}{r} \exp[-i\mathbf{k}_i \cdot \mathbf{r} - iE_{\tau i} t]. \quad (23)$$

⁹ R. G. Breene, Jr., Phys. Rev. **111**, 1111 (1958); **113**, 809 (1959); **119**, 1615 (1960).

In this equation each term is an exact solution to the Schrödinger equation for infinite separation of the proton-molecule system. The subscript i runs over the states of the molecule. When Eq. (23) is substituted into the Schrödinger equation—whose Hamiltonian is again given by Eq. (10)—all terms save the following drop out:

$$\begin{aligned} & \sum c_i(t) \exp[-iE_{\tau i} t] H' \varphi_i(\mathbf{r}_m) \frac{1}{r} \exp[i\mathbf{k}_i \cdot \mathbf{r} - iE_{\tau i} t] \\ &= i \sum \dot{c}_i(t) \exp[-iE_{\tau i} t] \varphi_i(\mathbf{r}_m) \frac{1}{r} \\ & \quad \times \exp[i\mathbf{k}_i \cdot \mathbf{r} - iE_{\tau i} t]. \quad (24) \end{aligned}$$

The k_i is negative for $i=1$ and positive of various values for all other i . The normality condition for the wave function is

$$(\Psi^*, \Psi) = \sum c_i^* c_i = 1. \quad (25)$$

The general form for the state growth coefficient is taken as follows:

$$c_i = \rho_i e^{i\omega_i t}. \quad (26)$$

At minus infinity of time the coefficient corresponding to the molecular ground state is again unity. We are next concerned with the value of same upper state coefficient after an infinite time. Initially we let

$$C_i = c_i \exp[i\mathbf{k}_i \cdot \mathbf{r}]. \quad (27)$$

We now multiply Eq. (24) through on the left, first by

$$\varphi_1^* r \exp[-(E_1 + E_{\tau 1})t],$$

then by

$$\varphi_2^* r \exp[-(E_2 + E_{\tau 2})t],$$

and so on. The result is

$$\sum C_i H_{1i}' = i\dot{C}_1, \quad (28a)$$

$$\sum C_i H_{2i}' = i\dot{C}_2, \quad (28b)$$

$$\sum C_i H_{3i}' = i\dot{C}_3, \quad (28c)$$

etc.

Equations (28) are added to obtain

$$\sum_j \sum_i C_i H_{ji}' = i \sum_i \dot{C}_i. \quad (29)$$

Equation (29) may be rewritten as follows:

$$\sum_i [C_i \sum_j H_{ji}' - i\dot{C}_i] = 0. \quad (30)$$

There are two ways in which this equation could hold. Either some linear combination of the terms in the sum is zero or each term is zero. At some point a great distance from the molecule both the matrix elements and the time rate of change of the coefficient in a given term will be zero. Hence, it follows that Eq. (30) is zero because each term in Eq. (30) is zero.

The impact parameter treatment is introduced, and Eq. (30) may be written as

$$\frac{dC_i}{dx} = -\frac{i}{v} \sum_j H_{ji}' \cdot C_j. \quad (31)$$

Equation (31) has the familiar and immediate solution:

$$C_i = e^{-iQ}, \quad Q = -i \int_{-\infty}^x \frac{1}{v} \sum_j H_{ji}' dx. \quad (32)$$

Relationships among the ρ_i and ω_i are required for the completion of the calculation. We begin by forming the column matrix which we term the amplitude matrix:

$$\mathbf{a} = (\rho_i e^{-i\omega_i}). \quad (33)$$

With this definition the Schrödinger equation may be written in matrix form as follows:

$$\mathbf{H}\mathbf{a} = i \frac{d}{dt} \mathbf{a}. \quad (34)$$

We multiply this equation through on the right by the associate matrix \mathbf{a}^\dagger to obtain

$$\mathbf{H}\mathbf{a}\mathbf{a}^\dagger = i \left(\frac{d}{dt} \mathbf{a} \right) \mathbf{a}^\dagger. \quad (35)$$

The product of the matrix \mathbf{a} and its associate may be written as follows:

$$\mathbf{a}\mathbf{a}^\dagger = \mathbf{b}. \quad (36)$$

This matrix possesses no inverse, and its adjoint matrix is a null matrix. However, we may form the pluserve matrix which, when it multiplies the matrix on the right, yields the null matrix.

In proving this the elements of the pluserve matrix are first defined as

$$b_{ii}^\S = \sum_{j \neq i} b_{jj}, \quad (37a)$$

$$b_{ij}^\S = -b_{ij}. \quad (37b)$$

A typical element of the $\mathbf{b}\mathbf{b}^\S$ product matrix can be

written as

$$\begin{aligned} b_{ij} &= a_{i1} a_{j1}^\dagger = \rho_i \rho_j, \\ c_{in} &= (\mathbf{b}\mathbf{b}^\S)_{in} = \rho_i \rho_n \sum_{i \neq n}' \rho_i^2 - \sum_{i \neq n}' \rho_i \rho_i^2 \rho_n \\ &= \rho_i \rho_n [\sum' \rho_i^2 - \sum' \rho_i^2] = 0, \end{aligned} \quad (38)$$

which demonstrates the result.

We multiply Eq. (35) through on the right to obtain the following:

$$i \left(\frac{d}{dt} \mathbf{a} \right) \mathbf{a}^\dagger \mathbf{b}^\S = \mathbf{0}. \quad (39)$$

As an example we treat the two-state case. The coefficient matrix and the product of this matrix with its associate are

$$\mathbf{a} = \begin{pmatrix} \rho_1 e^{-i\omega_1} \\ \rho_2 e^{-i\omega_2} \end{pmatrix}, \quad \mathbf{b} = \mathbf{a}\mathbf{a}^\dagger = \begin{pmatrix} \rho_1^2 & \rho_1 \rho_2 \\ \rho_1 \rho_2 & \rho_2^2 \end{pmatrix}. \quad (40)$$

We may form \mathbf{b}^\S through Eqs. (37) as

$$\mathbf{b}^\S = \begin{pmatrix} \rho_2^2 & -\rho_1 \rho_2 \\ -\rho_1 \rho_2 & \rho_1^2 \end{pmatrix}. \quad (41)$$

The matrix manipulation indicated by Eq. (39) next leads to two equations in the amplitudes and phases. We simply suppose there to be a constant difference between the two phases. This leads to the following expression:

$$e^{-i(\omega_1 - \omega_2)} = a + ib = (1 - b^2)^{1/2} + ib. \quad (42)$$

Equation (42) now allows us to write down one of the two equations arising from Eq. (39) as

$$\begin{aligned} \rho_1 \rho_1 \rho_2^2 [1 - (1 - b^2)^{1/2} - ib] \\ + i\omega \rho_1^2 \rho_2^2 [-1 + (1 - b^2)^{1/2} + ib] = 0. \end{aligned} \quad (43)$$

The solution is

$$b = 1. \quad (44)$$

The normality condition, of course, leads immediately to the relationship among the amplitudes, and we have obtained the same result which was obtained in the previous section in a somewhat more straightforward, if less generally applicable, manner.

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