

¹⁷I thank Professor L. Spruch for the argument on the elastic scattering threshold law which was given in a seminar at the Boulder Summer School, 1968 (unpublished). The analogy between our problem and this argument lies in the fact that in both cases we have two terms which we know at zero energy and from this we determine the k dependence of one part which is of interest. The analogy is, however, limited to this aspect because the way the two terms arise and the reason for our interest in one of them are quite different in the two problems.

¹⁸R. Peterkop, *Latvijas PSR Zinatnu Akad. Vestis* **9**, 79 (1960); also R. Peterkop and A. Liepinsh, *Ref. 3*, Eq. (12). See also the discussion after Eq. (11') in Sec. VI.

¹⁹That the classical derivation gives the correct threshold law even though, at first sight, one expects WKB and classical analyses to break down near threshold is because of the long-range nature of the Coulomb potential. In the Coulomb zone, the potential leads to characteristic $\exp[i(8ZR)^{1/2}]$ oscillations, i.e., relatively rapid oscillations. Outside this region, the wavelength of the oscillations becomes k^{-1} . Thus when $k \rightarrow 0$ even though the latter wavelength becomes large, the important point is that the Coulomb zone expands, stretching to $R = \infty$ at threshold. This statement is expressed mathematically by saying that

$$\frac{d\lambda}{dR} = \frac{d}{dR} \left(k^2 + \frac{2\xi Z}{R} \right)^{-1/2}$$

is much larger than unity for all values of large R . The argument that, paradoxically, a WKB treatment becomes better near threshold should be expected to be valid for any long-range force (at least for $l=0$ states. For non-s states, there will be a repulsive angular momentum potential far out which may limit the argument to potentials with r^{-n} , $n < 2$) and may be of interest particularly for systems in which polarizability dominates the threshold behavior.

²⁰J. W. McGowan, *Science* **167**, 1083 (1970), and references therein.

²¹I. Vinkalns and M. Gailitis, in *Proceedings of the*

Fifth International Conference on the Physics of Electronic and Atomic Collisions, Leningrad, 1967 (Leningrad Nauka, Leningrad, 1967), p. 648.

²²This imaginary potential adds to the angular momentum giving an effective complex angular momentum, somewhat like the Damburg-Gailitis effect for $e+H$ scattering below an excitation threshold. This suggests that this potential may be a manifestation of the doubly excited states with large dimensions.

²³Neglect of the R^{-2} term relates to the earlier remark (Ref. 11) that the restriction to $L=0$ is not crucial for the threshold law. In our derivation, the threshold law follows from the behavior in the Coulomb zone where the $1/R$ and $R^{-3/2}$ potentials dominate any R^{-2} potential due to non-S states.

²⁴It is instructive to examine Eq. (11') for the light it throws on Coulomb functions normalized per unit energy. This equation with $a=b=0$ gives in the Coulomb zone $\chi(R) = R^{1/4}$, whereas in the asymptotic limit it gives $k^{-1/2}$. This expresses the fact that energy-normalized functions $R^{-1/2} J_{2l+1}(8ZR)^{1/2}$, which are independent of energy in the Coulomb zone, connect to the asymptotic form $R^{-1} k^{-1/2} \exp[ikR + (iZ/k) \ln 2kR]$, which is more easily recognized to be an energy-normalized form because spherical waves normalized per unit energy, i.e., $k^{1/2} j_l(kr)$, have exactly the same form at ∞ except for the phase.

²⁵See Ref. 6, Eq. (15.3.14).

²⁶H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms* (Springer, Berlin, 1957).

²⁷The k^2 expansion in (A7) has been derived in many different ways. See, for instance, F. L. Yost, J. A. Wheeler, and G. Breit, *Phys. Rev.* **49**, 174 (1936); J. G. Beckerley, *ibid.* **67**, 11 (1945); and M. Abramowitz, *J. Math. Phys.* **33**, 111 (1954). The two derivations we present are both simple and of interest in their close connection to the two-electron wave functions and for seeing the passage from the Coulomb to the far zone.

Optical Potential for the Rotational Excitation of Diatomic Molecules by Atoms*

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By restricting attention to a single open scattering channel at a time, it is found that an optical potential, accurate to second order in the scattering potential, can be easily derived for the example of rotational excitation of a rigid rotator by a structureless atom. The resulting equations are contrasted with those derived from the close-coupling method. In cases where many open channels are present, the optical-potential method seems to offer many advantages over close coupling. Various practical methods for improving the accuracy of the optical potential beyond second order are discussed.

I. INTRODUCTION

The close-coupling method of Massey and Mohr¹

has received widespread attention ever since digital computers have made feasible the solution of many simultaneous ordinary differential equations. The

electron-hydrogen scattering problem has probably been the most thoroughly investigated using this method²; reasonable results can be obtained by using a few terms in the expansion of the total wave function.^{3,4}

In problems of more complexity, such as atoms colliding with molecules, one cannot hope to escape with only a small number of terms. Lester and Bernstein⁵ have described the computation procedures for a structureless atom incident on a rigid rotator. They solved up to 25 simultaneous second-order equations for this single problem to obtain results of high precision, but they make it clear that the close-coupling method is not practical in systems that have many degrees of freedom; one soon runs out of storage and computer costs are far too high.

The purpose of this paper is to investigate what can be done using complex potentials to replace the simultaneous equations of the close-coupling procedure. We shall confine our attention to the case of a structureless atom colliding with a rigidly rotating diatomic molecule, although the method is easily generalized.

II. DERIVATION OF OPTICAL POTENTIAL

We imagine a structureless atom of mass m incident upon a structureless homonuclear diatomic molecule whose moment of inertia is I . The Schrödinger equation we wish to deal with is

$$[T_R + H_{\text{rot}} + V(\vec{R}, \omega)] \Psi(\vec{R}, \omega) = E \Psi(\vec{R}, \omega). \quad (1)$$

In Eq. (1), the atomic coordinate is $\vec{R} \equiv (\rho, \Omega)$ in the center-of-mass system with $\Omega \equiv (\theta, \varphi)$, the rotator angle is $\omega \equiv (\xi, \eta)$, the relative kinetic energy is $T_R \equiv -(\hbar^2/2\mu)\nabla_R^2$, the molecule's rotational Hamiltonian is H_{rot} , and the interaction potential is V . The reduced mass of the system is μ .

We shall adopt the notation that wave functions represented by angular brackets belong to the rotator:

$$H_{\text{rot}} |jm_j\rangle = (\hbar^2/2I)j(j+1) |jm_j\rangle \equiv E_j |jm_j\rangle. \quad (2)$$

We wish to derive an equation from Eq. (1) which gives the wave function for a particular open channel, one whose rotator angular momentum is asymptotically j_a . We may choose j_a to be any rotator state which is energetically available. Asymptotically, the wave function for this channel is $\sum_{m_a} |j_a m_a\rangle \langle j_a m_a | \Psi(\vec{R}, \omega)$. If we let $P \equiv \sum_{m_a} |j_a m_a\rangle \langle j_a m_a |$, then the wave function can be written as $P\Psi$. The equation for $P\Psi$ is the Feshbach equation⁶

$$(PHP + P\hat{V}P - E) P\Psi = 0, \quad (3)$$

where

$$H = T_R + H_{\text{rot}} + V, \quad (4)$$

$$P\hat{V}P = PHQ [Q(E - H)Q]^{-1} QHP, \quad (5)$$

and $Q \equiv 1 - P$. Since $PQ = 0$ and $[P, T_R] = [P, H_{\text{rot}}] = 0$, Eq. (5) can be written as

$$(T_R + PVP + P\hat{V}P + E_{j_a} - E) P\Psi = 0, \quad (6)$$

where

$$P\hat{V}P = PVQ [Q(E - T_R - H_{\text{rot}} - V)Q]^{-1} QVP \quad (7)$$

is the optical potential. For simplicity, we specialize the argument to the elastic channel. The optical potential for inelastic channels will be treated in a separate paper. As in the close-coupling method, it is useful to use wave functions of definite total angular momentum J , composed of j_a and l' , the angular momentum of the atom-rotator relative motion⁵:

$$\begin{aligned} P\Psi^{JM}(\vec{R}, \omega) &\equiv \sum_{m_a} Y_{j_a m_a}(\omega) \psi_a^{JM}(\vec{R}) \\ &= \sum_{m_a} Y_{j_a m_a}(\omega) \sum_{l' m_{l'}} \rho^{-1} u_{al'}^J(\rho) Y_{l' m_{l'}}(\Omega) \\ &\quad \times (-1)^{j_a + l' + M} (2J + 1)^{1/2} \begin{pmatrix} j_a & l' & J \\ m_a & m_{l'} & -M \end{pmatrix}, \quad (8) \end{aligned}$$

where $\psi_a^{JM}(\vec{R}) \equiv \langle j_a m_a | \Psi^{JM}(\vec{R}, \omega) \rangle$. The large brackets are 3- j symbols. In addition, we use the expansion for cylindrically symmetric potentials

$$V(\vec{R}, \omega) = \sum_{t m_t} \frac{4\pi}{2t + 1} v_t(\rho) Y_{t m_t}^*(\Omega) Y_{t m_t}(\omega). \quad (9)$$

The projection operator Q is represented in terms of rotator eigenfunctions,

$$Q = \sum'_{j m_j} |j m_j\rangle \langle j m_j|, \quad (10)$$

where the prime, here and henceforth, signifies that the terms $P = \sum_{m_a} |j_a m_a\rangle \langle j_a m_a|$ are missing. A highly tractable approximation to the Green's function $[Q(E - T_R - H_{\text{rot}} - V)Q]^{-1}$ is obtained when V is neglected; this is the first term in a systematic expansion in powers of V . In this approximation, the Green's function can be written as

$$G_a^0(\vec{R}, \omega; \vec{R}', \omega') = \sum'_{j m_j} |j m_j\rangle \frac{e^{ik_j |R - R'|}}{|R - R'|} \langle j m_j|, \quad (11)$$

where

$$k_j = \begin{cases} \kappa_j & \text{for } E \geq E_j \\ i\kappa_j & \text{for } E < E_j \end{cases} \quad (12)$$

and

$$\kappa_j \equiv [(2\mu/\hbar^2) |E - E_j|]. \quad (13)$$

Finally, we shall make use of the expansion⁷

$$\exp(ik_j |R - R'|) (|R - R'|)^{-1} = 4\pi i k_j$$

$$\times \sum_{\lambda} j_{\lambda}(k_j \rho_{<}) h_{\lambda}^{(1)}(k_j \rho_{>}) \sum_{\mu} Y_{\lambda\mu}^*(\Omega) Y_{\lambda\mu}(\Omega'), \quad (14)$$

where $\rho_{<}$ and $\rho_{>}$ are the lesser and greater of ρ and ρ' , respectively, j_{λ} is the usual Bessel function, and $h_{\lambda}^{(1)} = j_{\lambda} + i n_{\lambda}$, where n_{λ} is the Neumann func-

tion.⁸ Equations (8) through (14) are now inserted into Eq. (6). The resulting equation is multiplied through by $Y_{lm}^*(\Omega)$ and $\langle j_a m_a |$, integrated over Ω and ω , and all the Racah algebra⁹ is carried out to obtain

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} \right) + E_{j_a} - E \right] u_{at}^j(\rho) + \sum_{l't'} f_{l't'}(J l j_a) v_t(\rho) u_{at}^j(\rho) + \sum_j' \sum_{\lambda t t' l' t'} g_{\lambda t t' l' t'}^j(J l j_a) \int [U_{\lambda t t'}^j(\rho, \rho') + i W_{\lambda t t'}^j(\rho, \rho')] u_{at}^j(\rho') \rho'^2 d\rho' = 0, \quad (15)$$

where

$$f_{l't'}(J l j_a) \equiv (-1)^{J+l+t'} \frac{2j_a+1}{2J+1} [(2l+1)(2l'+1)]^{1/2} \left\{ \begin{matrix} j_a & t & j_a \\ l & J & l' \end{matrix} \right\} \left\{ \begin{matrix} j_a & t & j_a \\ 0 & 0 & 0 \end{matrix} \right\} \left\{ \begin{matrix} l & t & l' \\ 0 & 0 & 0 \end{matrix} \right\}, \quad (16)$$

$$g_{\lambda t t' l' t'}^j(J l j_a) \equiv (4\pi)^{-1/2} (-1)^{t+t'} [(2j_a+1)(2J+1)(2\lambda+1)] [(2l+1)(2l'+1)]^{1/2} \times \left\{ \begin{matrix} j_a & J & l \\ \lambda & t & j \end{matrix} \right\} \left\{ \begin{matrix} j_a & J & l' \\ \lambda & t' & j \end{matrix} \right\} \left\{ \begin{matrix} \lambda & t & l \\ 0 & 0 & 0 \end{matrix} \right\} \left\{ \begin{matrix} \lambda & t' & l' \\ 0 & 0 & 0 \end{matrix} \right\} \left\{ \begin{matrix} j_a & t & j \\ 0 & 0 & 0 \end{matrix} \right\} \left\{ \begin{matrix} j_a & t' & j \\ 0 & 0 & 0 \end{matrix} \right\}, \quad (17)$$

$$U_{\lambda t t'}^j(\rho, \rho') \equiv -v_t(\rho) v_{t'}(\rho') [j_{\lambda}(\kappa_j \rho_{<}) n_{\lambda}(\kappa_j \rho_{>}) \theta(j_0 - j) - j_{\lambda}(i \kappa_j \rho_{<}) h_{\lambda}^{(1)}(i \kappa_j \rho_{>}) \theta(j - j_0 - 1)], \quad (18)$$

and

$$W_{\lambda t t'}^j(\rho, \rho') \equiv v_t(\rho) v_{t'}(\rho') j_{\lambda}(\kappa_j \rho) j_{\lambda}(\kappa_j \rho') \theta(j_0 - j). \quad (19)$$

The large curly brackets are 6- j symbols. In Eqs. (18) and (19), the function $\theta(n)$ is used to control the range of the index j in various parts of the optical potential:

$$\theta(n) = \begin{cases} 1 & \text{for } n \geq 0 \\ 0 & \text{for } n < 0. \end{cases} \quad (20)$$

The angular momentum j_0 is the highest rotator state that is energetically available; that is, any rotator state higher than j_0 is in a closed channel.

The second term in Eq. (15) is of the type found in close-coupling calculations. The multipoles of the potential serve to couple various partial waves of the relative motion so that the total angular momentum is always J while the rotator is always in the state J_a . The final term in Eq. (15) is from the optical potential. From Eq. (18) we see that the real portion U has two parts. The first part is due to second-order interactions with rotator states that are energetically available ($j \leq j_0$). After interaction, the final rotator momentum is j_a . The second term in Eq. (18) is the result of interactions with the closed channels ($j > j_0$); it is due to polarization or the virtual admixture of states during the interaction process. It is short ranged, as can be verified by noting the behavior of the Bessel and Hankel functions of imaginary

argument.

The imaginary or absorptive part W , given in Eq. (19), is due to excitation of open channels other than the one belonging to j_a .

The real and imaginary parts of the optical potential are separated easily, as shown in Eq. (15), when it is recognized that for real x and y , the product $j_{\lambda}(ix) h_{\lambda}^{(1)}(iy)$ is real for all λ , and that $j_{\lambda}(x) h_{\lambda}^{(1)}(y) = j_{\lambda}(x) j_{\lambda}(x) + i j_{\lambda}(x) n_{\lambda}(x)$.

The clean break between real and imaginary parts is due to one device: use of the free-particle Green's function. Had the Green's function been composed of eigenfunctions of the entire Hamiltonian in Eq. (1) in the usual manner, the separation of the optical potential into real and imaginary parts could have been accomplished only in a symbolic way.

We now address the question of the range over which the approximation may be expected to yield reasonably accurate results. We assume the potential to be of the usual form

$$V = V_0(\rho) [1 - a P_2(\cos \xi)],$$

where $\xi \equiv \Omega - \omega$ and a is the asymmetry factor. We see from Eq. (7) that the optical potential is zero for the symmetric part of V (because $PQ=0$), so that $P\hat{V}P \sim a^2 V_0$. This must be compared with the second term in Eq. (6), which is exact. It is of the order of V_0 and dominates the elastic scattering providing $a^2 \ll 1$. Thus we can say that elastic scattering will be accurately represented provided this criterion is met.

For the inelastic channel, the situation is more complicated, since there is no dominating exact term. Equation (7) is expanded:

$$P\hat{V}P = PVQ[G_a^0 + G_a^0 V G_a^0 + \dots] QVP,$$

where G_a^0 is defined in Eq. (11). Since our approximation involves retaining only the first term, we must examine under what conditions such an expansion converges rapidly. Strictly speaking, since one is expanding $[1 - G_a^0 V]^{-1}$ in a Neumann series, one should solve the eigenvalue problem¹⁰

$$G_a^0 V\chi = \lambda\chi.$$

The rate of convergence of the expansion is then $|\lambda_{\max}|$. Our approximation is good if $|\lambda_{\max}| \ll 1$. In general, it is not practical to find these eigenvalues, so estimates must be resorted to; one obtains a small $|\lambda_{\max}|$ if $E \gg |\epsilon|$, where ϵ is the strength of the interaction. The strength may be defined so that $\epsilon V'(\rho) = V_0(\rho)$, where $\int |V'(\rho)| d\rho = 1$. If $V_0(\rho)$ has a $1/\rho$ singularity, ϵ can be defined such that $\rho V'(\rho) \rightarrow 1$ as ρ goes to zero. These crude estimates are usually very conservative; that is, $|\lambda_{\max}|$ is usually much less than $|\epsilon|/E$. Better estimates have been discussed by Kohn.¹⁰

In general, the approximation becomes better as the incident energy becomes greater and, incidentally, as the close-coupling method becomes more cumbersome.

III. COMPARISON WITH CLOSE-COUPPLING EQUATIONS

The close-coupling equations for the atom-rotator problem are⁵

$$\left[-\frac{\hbar^2}{2\mu} \left(\frac{d^2}{d\rho^2} - \frac{l(l+1)}{\rho^2} \right) + E_L - E \right] u_{Ll}^J(\rho) + \sum_{L'l't} \hat{f}_{L'l't}(JLl) v_t(\rho) u_{L'l't}^J(\rho) = 0, \quad (21)$$

where

$$\hat{f}_{L'l't}(JLl) \equiv (-1)^{J+l'} \frac{2L'+1}{2J+1} [(2l+1)(2l'+1)]^{1/2} \times \begin{Bmatrix} L & t & L' \\ l & J & l' \end{Bmatrix} \begin{pmatrix} L & t & L' \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l & t & l' \\ 0 & 0 & 0 \end{pmatrix}. \quad (22)$$

In the above, L is the rotator angular momentum, while, as before, l and J are the orbital angular momentum of the relative motion and the total angular momentum, respectively. Equations (21) are to be compared with Eqs. (15).

The easy comparisons tend not to be in favor of the optical equations. The optical equations we have derived are accurate only to second order, while, in principle, the close-coupling equations are exact. Even without exchange, the optical equations are nonlocal; the close-coupling equa-

tions are not. We do not view the latter point as serious, since the technique for numerically solving nonlocal equations in a noniterative manner is well known (see Marriotti²).

In the close-coupling scheme, a differential equation for every open channel is required as a minimum. The number of differential equations required to represent the closed channels accurately is a matter of technique; various methods have been suggested and investigated by Burke and co-workers^{9,11} and by Rotenberg.¹² The main criticism of the close-coupling method is that it gives far too much information: It yields the entire S matrix whether it is wanted or not. In the face of many open channels this can be a serious computational drawback. It is often the case that one wishes to know only what flux is being taken out of the incident beam, and what flux is being injected into a few interesting channels. The optical equations yield only the required information.

For every total angular momentum J , the number of differential equations required by the close-coupling method is the number of combinations of L and l allowed by the triangle relations. This number is $J^2 + 2J$ provided each closed channel is represented by a differential equation also. The number of equations required by the optical equations is less because L is held fixed at j_a , and is only the number of l 's that satisfy $|j_a - J| \leq l \leq j_a + J$, which is $2j_a + 1$ or $2J + 1$, whichever is smaller. This number of equations must be multiplied by 2 because the optical equations are complex. This comparatively small set of equations need be solved only for each channel of interest.

There is a final advantage to the optical equations which offsets the fact that they are nonlocal, and that is that they are all of the open-channel variety. Consequently, only outward numerical integrations need be performed. Much computer time is used in solving the closed-channel equations in the close-coupling method to ensure their proper behavior at infinity.²

In particular, if the incoming channel is denoted by the rotator angular momentum j and the orbital angular momentum l , and the outgoing channel by primed quantities, then asymptotically all solutions to Eq. (15) behave as

$$u_{j'l't}^J(\rho) \sim \delta_{jj'} \delta_{l'l'} \delta_{t't} (k_j \rho) + (k_j/k_{j'})^{1/2} \times T^J(jl; j'l') h_l^{(1)}(k_j \rho),$$

where the transition matrix is complex:

$$T^J(jl; j'l') = i^J(jl; j'l') + i \tau^J(jl; j'l').$$

The elastic cross section is given by¹³

$$\sigma(j \rightarrow j) = \frac{\pi}{(2j+1)k_j^2} \sum_{J=0}^{\infty} \sum_{l, l'} (2J+1) |T^J(jl; j'l')|^2,$$

where $|J-j| \leq l \leq J+j$, and similarly for l' . The excitation cross section is

$$\sigma(j \rightarrow j') = \frac{\pi}{(2j+1)k_j^2} \sum_{J=0} \sum_l \sum_{l'} (2J+1) |T^J(jl; j'l')|^2,$$

where $|J-j| \leq l \leq J+j$ and $|J-j'| \leq l' \leq J+j'$. The total cross section is

$$\sigma_T = \frac{\pi}{(2j+1)k_j^2} \sum_{J=0} \sum_l \sum_{l'} (2J+1) \tau^J(jl; j'l'),$$

and therefore the absorption cross section is $\sigma_T - \sigma(j \rightarrow j)$. At the origin all $u_{ji}^J = 0$.

IV. OTHER APPROXIMATIONS TO GREEN'S FUNCTION

In the approximation presented in this paper, it is a simple matter to write down the optical equations for almost any nonionizing and nondissociating binary collision. The Green's function is always of the form

$$G_a^0(\vec{R}, \vec{r}; \vec{R}', \vec{r}') = Q \sum_j \Phi_j(\vec{r}) \frac{e^{ik_j|\vec{R}-\vec{R}'|}}{|\vec{R}-\vec{R}'|} \Phi_j^*(\vec{r}') Q, \quad (23)$$

where the $\Phi_j(r)$ are the product eigenfunctions of the noninteracting systems, $k_j \sim (E - E_j)^{1/2}$, and E_j is the energy required to excite the state j . As before, $Q \equiv \sum_{jm} |jm\rangle \langle jm|$ projects away the terms referring to the channel of interest. Higher Born approximations are of course possible, but they are not computationally useful. In this section, we shall indicate a few ways in which it may be possible to improve upon Eq. (23) with reasonable labor. We deal mainly with the atom-rotator case.

A. High-Energy Approximation

In this approximation, we seek a function $S_j(\vec{R}, \omega)$ which satisfies

$$(T_R + H_{\text{rot}} + V - E) Y_{jm}(\omega) e^{i\vec{k}_j \cdot \vec{R}} e^{S_j(\vec{R}, \omega)} = 0. \quad (24)$$

The equation for S_j is

$$(\hbar^2/2\mu) [2ik_j \cdot \vec{\nabla}_R S_j + \vec{\nabla}_R^2 S_j - (\vec{\nabla}_R S_j)^2] + (\hbar^2/2I) [\vec{\nabla}_\omega^2 S_j - (\vec{\nabla}_\omega S_j)^2] = V(\vec{R}, \omega). \quad (25)$$

The solution to (25) can be approximated in a number of ways depending on the physical situation. For example, if S_j is considered a first-order quantity (in powers of V) and if μ is large compared to I/R_0^2 (R_0 is the dimension of the rotator), then the equation emerging from (25) is

$$H_{\text{rot}} S^{(1)}(\vec{R}, \omega) = V(\vec{R}, \omega), \quad (26)$$

being independent of j in this approximation.

We expand

$$S^{(1)} = \sum_{tm_t} \frac{4\pi}{2t+1} s_t^{(1)}(\rho) Y_{tm_t}^*(\Omega) Y_{tm_t}(\omega) \quad (27)$$

and insert this and the expansion of $V(\vec{R}, \omega)$, Eq. (9), into (26) to obtain

$$s_t^{(1)}(\rho) = \frac{2I}{\hbar^2} \frac{v_t(\rho)}{t(t+1)}, \quad t > 0 \quad (28a)$$

$$s_0^{(1)}(\rho) = 0, \quad t = 0. \quad (28b)$$

The new Green's function now reads

$$G_a^1 = \sum'_{jm'_j m'_j} Y_{jm'_j}(\omega) e^{S(\vec{R}, \omega)} \frac{e^{ik_j|\vec{R}-\vec{R}'|}}{|\vec{R}-\vec{R}'|} \times e^{S^*(\vec{R}', \omega')} Y_{jm'_j}^*(\omega')$$

or, upon expanding the exponential containing S and using Eq. (11), we have

$$G_a^1 = G_a^0 + \left[\sum'_{qm_q} \sum_{jm_j} \sum_t \frac{1}{t(t+1)} [(2j+1)(2q+1)]^{1/2} \times \begin{pmatrix} j & t & q \\ m_j & -(m_j+m_q) & m_q \end{pmatrix} \begin{pmatrix} j & t & q \\ 0 & 0 & 0 \end{pmatrix} \times \frac{e^{ik_j|\vec{R}-\vec{R}'|}}{|\vec{R}-\vec{R}'|} [v_t(\rho) Y_{qm_q}(\omega) Y_{jm_j}(\Omega) + v_t(\rho') Y_{qm_q}^*(\omega') Y_{jm_j}^*(\Omega')] \right], \quad (29)$$

which shows the first-order correction explicitly.

B. Adiabatic Approximation

If the atom moves slowly compared to the rotational motion of the molecule, we can define adiabatic states by

$$[H_{\text{rot}} + V(\vec{R}, \omega)] \Phi_j(\vec{R}, \omega) = \mathcal{E}_j(\vec{R}) \Phi_j(\vec{R}, \omega), \quad (30)$$

where \vec{R} is considered a parameter.

Equation (30) can be solved by matrix methods¹⁴ or variational techniques. In any event, we shall assume the Φ_j are known and we seek solutions to Eq. (1) in the form $F_j(\vec{R}) \Phi_j(\vec{R}, \omega)$, with the result

$$[E - \mathcal{E}_j(\vec{R}) - T_R] F_j(\vec{R}) = 0, \quad (31)$$

where the Born-Oppenheimer terms have been neglected. In order to recover the desired form of the Green's function, $F_j(\vec{R})$ must be replaced by a plane wave, or, equivalently, $\mathcal{E}_j(\vec{R})$ must be replaced by a constant. To satisfy the proper boundary conditions at infinity, we choose this constant to be $\mathcal{E}_j(\infty) = E_j$, the asymptotic rotational energy for the state j . We now expand

$$\Phi_j(\vec{R}, \omega) = \sum_{j'm'_j} \varphi_{jj'}(\rho) Y_{j'm'_j}^*(\Omega) Y_{j'm'_j}(\omega) \quad (32)$$

and write the adiabatic Green's function as

$$G_a^2(\vec{R}, \omega; \vec{R}', \omega') = Q \sum_j \Phi_j(\vec{R}, \omega) + \sum_{j=j_1+1}^{\infty} \Phi_j(\vec{r}) e(\vec{k}, \vec{R}, \vec{R}') \Phi_j^*(\vec{r}'), \quad (34)$$

$$\begin{aligned} & \times \frac{e^{ik_j |\vec{R}-\vec{R}'|}}{|\vec{R}-\vec{R}'|} \Phi_j(\vec{R}', \omega') Q \\ & = \sum'_{j'm_j} \sum'_{j''m_j''} \sum_j \varphi_{jj'}(\rho) Y_{j'm_j}^*(\Omega) Y_{j''m_j''}(\omega) \\ & \times \frac{e^{ik_j |\vec{R}-\vec{R}'|}}{|\vec{R}-\vec{R}'|} Y_{j''m_j''}^*(\omega') Y_{j'm_j}(\Omega') \varphi_{jj''}^*(\rho'). \end{aligned} \quad (33)$$

We note the incompatibility of the adiabatic assumption and the replacement of $F_j(\vec{R})$ by a plane wave, and for this reason we do not place a great deal of confidence in Eq. (33).¹⁵

C. Closure Approximation

We refer to the Green's function in Eq. (23). It may happen that for some forms of the interaction the exponential can be legislated insensitive to j for j greater than some j_1 . That is, $k_j = \bar{k}$ for $j > j_1$, where \bar{k} is some average wave number. For convenience we denote the spherical wave as $e(k_j, \vec{R}, \vec{R}')$ and write Eq. (23) as

$$G_a^0 \approx Q \sum_{j=0}^{j_1} \Phi_j(\vec{r}) e(k_j, \vec{R}, \vec{R}') \Phi_j^*(\vec{r}') Q$$

where we have assumed that $j_1 > j_a$. If we add and subtract the missing terms from the second portion of (34), we find

$$\begin{aligned} G_a^0 & \approx \delta(\vec{r} - \vec{r}') e(\bar{k}, \vec{R}, \vec{R}') \\ & + Q \sum_{j=0}^{j_1} \Phi_j(\vec{r}) e(k_j, \vec{R}, \vec{R}') \Phi_j^*(\vec{r}') Q \\ & - \sum_{j=0}^{j_1} \Phi_j(\vec{r}) e(\bar{k}, \vec{R}, \vec{R}') \Phi_j^*(\vec{r}'), \end{aligned} \quad (35)$$

which is simpler to use because of the finite j sum. The problem, of course, is to find a "best" value of \bar{k} . In Coulomb interactions, if one is willing to ignore the continuum everywhere but in the completeness relation, then $k = [(2\mu/\hbar^2)(E - \epsilon_0)]^{1/2}$ for j_1 greater than a small integer, where ϵ_0 is the ground-state energy. If one does not have a spectrum which approaches a limit point, or if one wishes to include the continuum in finding \bar{k} , the problem is much more difficult, and is being addressed by us at present.

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