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MODIFIED METHOD OF PERTURBED STATIONARY STATES II. SEMICLASSICAL AND LOW-VELOCITY QUANTAL APPROXIMATIONS

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MODIFIED METHOD OF PERTURBED STATIONARY STATES
II. SEMICLASSICAL AND LOW-VELOCITY QUANTAL APPROXIMATIONS

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ABSTRACT

For one-electron heteropolar systems, the wave-theoretic Lagrangian of Paper I[2] is simplified in two distinct approximations. The first is semiclassical; the second is quantal, for velocities below those for which the semiclassical treatment is reliable. For each approximation, unitarity and detailed balancing are discussed. Then, the Variational Method as described by Demkov is used to determine the coupled equations for the radial functions and the Euler-Lagrange equations for the translational factors which are part of the theory. Specific semiclassical formulae for the translational factors are given in a many-state approximation. Low-velocity quantal formulae are obtained in a one-state approximation. The one-state results of both approximations agree with an earlier determination by Riley.

CONTENTS

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1. INTRODUCTION

This paper is concerned with elastic and inelastic collisions for one-electron heteronuclear diatomic systems. An example of current interest is C^{+}-H charge exchange at H-energies below about 25 keV.[1] The purpose of the paper is the derivation of specific scattering equations from the general theory developed in the companion paper I.[2] This new quantal theory takes cognizance of electron translational effects in a way which generalizes the approach of Bates and McCarroll.[3] The translational effects are accounted for by two state-dependent parameters which are determined variationally as functions of internuclear separation.

Two approximations are considered. The first is semiclassical; the second is a quantal approximation designed to cover impact energies too low for the semiclassical approximation. The value of these approximations is that they lead from the integro-differential equations of I[2] to ordinary differential equations of a familiar form and thus lend themselves to numerical applications. In each case the starting point is the quantal Lagrangian of I[2] and the first result is an approximate Lagrangian from which the equations for the radial scattering functions and translational parameters are then determined. The application of approximations to the system Lagrangian, rather than to the equations of motion, does not appear to be common in atomic scattering

theory. It was found to be helpful in developing a final set of approximate equations and conservation laws which were mutually compatible.

The semiclassical analysis (Section II) is based on the work of Riley.[4] A new generalization of this approach was devised to allow for the non-diagonality of the overlap matrix. This results from the appearance in the semiclassical theory of translational factors of the Bates-McCarroll type.[3] The final semiclassical coupled equations are very similar in form to those in current use. However, they differ from previous formulations in detail, because they involve the translational parameters mentioned above.

The many-state semiclassical determination of the translational parameters requires an additional approximation which is discussed in Section III. Parameters are obtained for either adiabatic or diabatic state expansions. In the separated-atom limit, but usually not elsewhere, the optimized parameters agree with the results of Bates and McCarroll. For a one-state expansion the variational result of Riley and Green is recovered.[5]

The low-velocity quantal approximation (Section IV) leads to coupled differential equations of the usual form for the radial scattering functions. In this approximation, no plane-wave translational factors appear in the matrix elements. However, the translational parameters appear as coefficients in combinations of matrix elements which, overall, determine

the coupling. These equations provide an alternative low-energy computational approach to that proposed by Thorson and Delos.[b] The translational parameters are optimized in a one-state approximation in Section V. In this formulation the forbidden region can be discussed. To get slowly varying solutions we average the high-frequency oscillations out of the parameter equations. The results are then in agreement with those based on semiclassical theory.

II. SEMICLASSICAL REDUCTION OF THE LAGRANGIAN

Consider the Lagrangian $\mathscr{L}$ defined in Eq. (69) of I.[2] Since $\mathscr{L}$ is diagonal with respect to the total angular momentum quantum number K, the superscript K on the radial scattering functions $R^K_{n\ell;G_{AB}}$ of I[2] can be suppressed. Also let $G \equiv n\ell$ and $G' \equiv G_{AB}$ so that G is the electronic state index and G' labels the initial conditions. Following a well-known line of argument, the radial functions $R_{GG'}$ are expanded in terms of in-out reference functions $F_G^{\mp}(x)$ defined in Eq. (1);

$$\frac{d^2}{dx^2} F_G^{\pm}(x) + K_G^2(x) F_G^{\pm}(x) = 0 ,$$

$$F_G^- \frac{d}{dx} F_G^+(x) - F_G^+ \frac{d}{dx} F_G^-(x) = 2i,$$

$$F_G^{\pm}(x)^* = F_G^{\mp}(x),$$

$$j_G(x) = \frac{-i}{2} (F_G^+ \overleftrightarrow{\frac{d}{dx}} F_G^-)(x). \qquad (1)$$

In Eq. (1) $K_G^2(x)$ is assumed to be given.

The last equation shows the relation of $F_G^{\pm}$ to the regular solution $\phi_G(x)$. In addition to Eqs. (1) the JWKB approximations

$$F_G^{\pm} \sim (K_G)^{-\frac{1}{2}} e^{\pm i(\phi_G + \frac{\pi}{4})},$$

$$\frac{dF_G^{\pm}}{dx} \sim \pm iK_G F_G^{\pm}, \tag{1a}$$

$$\phi_G(x) = \int_{T_G}^{x} dy K_G(y),$$

are used. The lower limit T_G is the outermost zero of $K_G(x)$. The radial scattering functions $R_{GG'}(\varepsilon_G)$ in $\mathscr{L}$ are expanded according to

$$R_{GG'}(\varepsilon_G) = C_{GG'}^{+}(\varepsilon_G)F_G^{+}(\varepsilon_G) + C_{GG'}^{-}(\varepsilon_G)F_G^{-}(\varepsilon_G), \tag{2}$$

and the condition

$$\frac{dC_{GG'}^{+}}{d\varepsilon_G} F_G^{+} + \frac{dC_{GG'}^{-}}{d\varepsilon_G} F_G^{-} = 0, \tag{3a}$$

is imposed so that

$$\frac{dR_{GG'}}{d\varepsilon_G} = C^{+}_{GG'}\frac{dF^{+}_{G}}{d\varepsilon_G} + C^{-}_{GG'}\frac{dF^{-}_{G}}{d\varepsilon_G}, \tag{3b}$$

$$\frac{d^2R_{GG'}}{d\varepsilon_G^2} = -K_G^2R_{GG'} \pm \frac{2i}{F^{\pm}_{G}}\frac{dC^{\pm}_{GG'}}{d\varepsilon_G}.$$

In order that $R_{GG'}$ be regular as $R \to 0$, Eq. (1) requires that as $R \to 0$

$$C^{+}_{GG'}(R) \to -C^{-}_{GG'}(R). \tag{4}$$

The amplitudes $C^{\pm}_{GG'}(R)$ will be considered to be defined at all R even though the expressions (1a) are not.

The semiclassical reduction of the quantal Lagrangian will now begin with the substitutions of the foregoing expressions for $R_{GG'}(\varepsilon_G)$ etc. into Eq. (I-69). Let

$$\mathscr{L} = (-1)^{\bar{M}_K}4\pi(2K+1)\delta_{K\bar{K}}\delta - M_K\bar{R}_K^L. \tag{5a}$$

Let $G = n,\Lambda$ as in paper I; let $\bar{G} = \bar{n},\bar{\Lambda}$ and $\tilde{G} = \bar{n},-\bar{\Lambda}$, where n numbers states with the same Λ. Then, noting that K_G, γ_G, and k_G depend only on $|\Lambda|$,

$$\mathcal{L} = \sum_{\bar{G}} \sum_{G} (-1)^{\bar{K}+K} \int_0^{\xi_G} d\xi_{\bar{G}} \left(C^{+}_{\bar{G}G}, (\xi_{\bar{G}}) F^{+}_{\bar{G}}(\xi_{\bar{G}}) + C^{-}_{\bar{G}G}, (\xi_{\bar{G}}) F^{-}_{\bar{G}}(\xi_{\bar{G}}) \right)$$

$$\times \int d\tau_G \rho_G d\rho_G J_G^{-1} A_{\bar{G}}(\rho_{\bar{G}} \tau_{\bar{G}}; \rho_G \tau_G) \left\{ d^{K}_{\Lambda\bar{\Lambda}}(\Theta_{10} - \bar{\Theta}_{10}) H^{K}_{GO} \right.$$

$$\left. + d^{K}_{\Lambda,-1} H^{K}_{G,-1} + d^{K}_{\Lambda,+1} H^{K}_{G1} \right\} \qquad (5b)$$

In Eqs. (5) the notation of paper I[2] is used. Bars distinguish the left-hand function from the right, $A_G(\rho_G, \tau_G; \xi_G)$ is the electronic fixed nucleus molecular eigenfunction without its normalized azimuthal part, and the $d^{K}_{\Lambda\bar{\Lambda}}$ are rotation matrices of argument defined in Eq. (68)[2]. The quantity J_G is the Jacobian of the transformation (41)[2].

The functions H^{K}_{GO} etc. are defined by

$$\frac{-2M}{\hbar^2} H^{K}_{G\pm1} = \pm\sqrt{K(K+1)} \left\{ \frac{1}{\xi_G^2} \left(\frac{\partial}{\partial \Theta_G} \mp \Lambda \cot\Theta_G \right) A_G R_{GG'}(\xi_G) \right. \qquad (6)$$

$$\left. + \frac{m}{M} \left(\frac{d\gamma_G}{dR} - k_G R \right) \frac{\rho_G}{\xi_G} A_G \left(C^{+}_{GG'} \frac{dF^{+}_{G}}{d\xi_G} + C^{-}_{GG'} \frac{dF^{-}_{G}}{d\xi_G} \right)(\xi_G) \right\} .$$

In Eqs. (5) and (6) m is the electron mass and M is the nuclear reduced mass. The scattering coordinate for the state G is ξ_G, and ρ_G, ϕ_G, τ_G, and Θ_G are body-fixed cylindrical or spherical coordinates of the electron

position vector $\vec{r}_G$. The body-fixed axes are defined from the spherical coordinate unit vectors for $\vec{r}_G$ in the usual way.

Finally,

$$\frac{-2M}{\hbar^2} V^K_{GG'} = \frac{2\pi A_G}{F_G^2} \frac{dC^{\pm}_{GG'}}{d\varepsilon_G}(\varepsilon_G) + 2\left(\frac{\partial \gamma_G}{\partial r_G} + R\left(\frac{d\gamma_G}{dR} + Rk_G\right)\frac{\partial A_G}{r_G}\right)$$

$$\times \left(C^{+}_{GG'}\frac{dF^{+}_G}{d\varepsilon_G} + C^{-}_{GG'}\frac{dF^{-}_G}{d\varepsilon_G}\right) + \left\{-K'_G + \gamma_G^2 + \frac{m}{M}\left(-K'_G - \frac{J(J+1)}{r_G^2}\right)\right.$$

$$\times \left(-\gamma_G^2 + 2k_G R(\varepsilon_G - R\gamma_G)\right) + \frac{m}{M}\left(-K'_G\right)\left(2R\frac{dk_G}{dR}(\varepsilon_G - R\gamma_G)\right.$$

$$\left.\left. - 2R\gamma_G\frac{d\gamma_G}{dR} - 4R^2\gamma_G k_G + R^4 k_G^2 + 2(k_G R - \frac{d\gamma_G}{dR})\gamma_G\right)\right\} \qquad (7)$$

$$\times A_G(\varepsilon_G, \gamma_G, r_G)(C^{+}_{GG'}, F^{+}_G + C^{-}_{GG'}, F^{-}_G)(\varepsilon_G) .$$

The terms in Eq. (6) are nominally rotational coupling terms; those in Eq. (7) are nominally radial coupling terms. However, the traditional selection rules on Λ apply through the d-matrices only in the limit of zero velocity. The terms where m/M appears are electron translation kinetic energy terms discussed in I.[2] In obtaining Eqs. (5) - (7) from Eq. (69) of I,[2] terms of the type $\partial^2 A_G/(\partial\varepsilon_G)^2$ etc. were dropped

as is customary in semiclassical approximations. Also, in the m/M terms of the first Eq. (71)[2], $\partial^2 R_{GG'}/(\partial\xi_G)^2$ was set equal to its large term $-K_G^2 R_{GG'}$. This modifies the $dC^{\pm}_{GG'}/d\xi_G$ terms by a negligible amount of order m/M compared to 1. In Eq. (7)

$$\kappa_G^2 = -\frac{K(K+1)\hbar^2}{r_G^2} + \frac{2M}{\hbar^2}\left(E - \mathcal{E}_G(r_G)\right), \tag{8}$$

where K is the total angular momentum quantum number, E the c.m. total energy, and $\mathcal{E}_G(r_G)$ the electronic eigenvalue including the nuclear repulsion. Later K_G^2 will be taken to be equal to κ_G^2. Also dropped from Eq. (69)[2] were kinetic energy terms of order (m/M) mv^2 and coupling terms of order (m/M)v compared to v, where v is the order of magnitude of the relative collision velocity. Finally m/M corrections to the potential energy were dropped, including the term Δv of Eq. (51)[2]. None of these simplifications should be detrimental in inelastic scattering applications.

As the next step, a basic approximation is introduced. We allow for the small difference O(m/M), between ξ_G and $\xi_{\bar{G}}$ only in the rapidly varying phase of the reference functions $F^{\pm}_G(\xi_G)$ and set $\xi_G = \xi_{\bar{G}}$ in the $C^{+}_{GG'}(\xi_G)$ and elsewhere, including the electronic eigenfunctions. The rationale is that in the classically allowed regions $F^{\pm}_G$ oscillates with wave number ~Mv/ħ while $C^{\pm}_{GG'}$ oscillates with wave number ~ $\mathcal{E}_G/(\hbar v)$. Multiplying each wave number by the order of magnitude $(m/M)a_0$ of the difference between ξ_G and $\xi_{\bar{G}}$ one obtains $mva_0/\hbar$ in the first instance and $\frac{m\mathcal{E}_G a_0}{\hbar^2} \times (\hbar/Mv)$ in the second. Here a_0 is the atomic unit of length.

The first result is of the order of the non-adiabatic coupling; the second is of the order $\mathcal{E}_G/E$ smaller and is neglected. Consistent with the high frequency-low frequency argument just introduced, the coupling between incoming and outgoing parts of $\mathcal{V}$ are neglected at this point and the coupling is taken into account only in the classically allowed regions where $K_G^2 > 0$. The JWKB approximations to $F_G^{\pm}$ are then introduced. This leads to

$$F_G^{\pm}(\vec{r}_G) = F_G^{\pm}(\vec{r}_{\bar{G}}) \, e^{\pm i K_G (r_G - r_{\bar{G}})} \,, \tag{9}$$

where from Eqs. (41)[2] it can be shown that

$$r_G - r_{\bar{G}} = \frac{m}{M}(\gamma_{\bar{G}} - \gamma_G) R + \frac{m}{M}\left[\gamma_{\bar{G}} - k_{\bar{G}} R^2 - (\gamma_G - k_G R^2)\right](\hat{R}\cdot\vec{r}) \,.$$

In Eq. (10) $\vec{r}$ locates the electron with respect to the center of mass of the nuclei and from Eq. (41) of I[2]

$$\vec{r}_G = \vec{r} + \gamma_G(R)\vec{R}, \tag{11}$$

$\hat{R}$ being the internuclear line from nucleus A to nucleus B. Using Eq. (68)[2] the uniform semiclassical approximation for the rotation matrices yields

$$d^K_{\Lambda+\tau\Lambda}(\theta_{10} - \theta_{1G}) = J_{\Lambda+\tau-\Lambda}\left((K+\tfrac{1}{2})\frac{m}{M}\frac{\mathcal{E}_G}{\xi_{\bar{G}}}(\gamma_{\bar{G}} - \gamma_G)\right). \tag{12}$$

The function $J_n(x)$ is Bessel's function and can be represented by

$$J_n(x) = \frac{i^{-n}}{2} \int_0^{2\pi} d\varphi\, e^{i(x\cos\varphi + n\varphi)} \qquad (13)$$

The next main step is to insert the JWKB approximations for $F_{\bar{G}}^{\pm}$ as well as Eqs. (12) and (13) for $d^{K}_{\ldots}$ into Eqs. (5) - (7). Neglect of the terms containing frequency sums in favor of frequency differences splits L into a sum, $L^{+} + L^{-}$. Introducing the definition $dv_{\bar{G}} = d\xi_{\bar{G}}$, the result for L^{+} is

$$L^{+} = -\frac{\hbar}{M} \sum_{\bar{G}} \sum_{G} (-i)^{\ldots} \int^{\infty} d\ldots_{\bar{G}}\, C^{-}_{G\bar{G}}\ldots(\xi_{\bar{G}}) e^{i(\ldots_G - \ldots_{\bar{G}})(\xi_{\bar{G}})}$$

$$\times \left[(K_G/K_{\bar{G}})^{\frac{1}{2}} \int dv_{\bar{G}}\, e^{i\Gamma_{\bar{G}G}} \chi_{\bar{G}}^{*} \chi_G\, i \frac{d}{d\xi_{\bar{G}}} \right.$$

$$+ (K_G/K_{\bar{G}})^{\frac{1}{2}} \int dv_{\bar{G}}\, e^{i\Gamma_{\bar{G}G}} \chi_{\bar{G}}^{*}\, i \left(\frac{\partial}{\partial \xi_G} + R \left(\frac{d\gamma_G}{dR} + Rk_G \right) \frac{\partial}{\partial \ldots_G} \right) \chi_G$$

$$\left. + (K_G K_{\bar{G}})^{-\frac{1}{2}} \frac{\sqrt{K(K+1)}}{\ldots_{\bar{G}}} \int dv_{\bar{G}}\, e^{i\Gamma_{\bar{G}G}} \chi_{\bar{G}}^{*} \frac{1}{2i} \left(L_{+G} - L_{-G} \right) \chi_G \right]$$

$$+ (K_G/K_{\bar{G}})^{\frac{1}{2}} \frac{\sqrt{K(K+1)}}{\xi_{\bar{G}}} \frac{m}{M}\left(\frac{d\gamma_G}{dR} - \gamma_G R\right) \int dv_{\bar{G}} e^{i\vec{\xi}_{\bar{G}}\cdot\vec{\eta}_G} \chi_{\bar{G}}^* \cos(\vec{\xi}_{\bar{G}}\cdot\vec{\eta}_G$$

$$+ (K_G K_{\bar{G}})^{-\frac{1}{2}} \left(\tfrac{1}{2}\right) \int dv_{\bar{G}} e^{i\vec{\xi}_{\bar{G}}\cdot\vec{\eta}_G} \chi_{\bar{G}}^* \{\text{Eq. (7)}\} \chi_G \Big] C^+_{GG'}(\xi_{\bar{G}}). \tag{14}$$

In Eq. (14) the complete molecular wave functions $\chi_G = (2\pi)^{-\frac{1}{2}} A_G \exp(i\vec{\eta}_G)$ have been reinstated. The formula for $\xi_{\bar{G}\bar{G}}$ is obtained by collecting phase factors from Eqs. (9) - (13):

$$\Gamma_{\bar{G}G} = (K+\tfrac{1}{2}) \frac{m}{M} \frac{D\xi\cos\zeta_{\bar{G}}}{\xi_{\bar{G}}} (\gamma_{\bar{G}} - \gamma_G) + K_G \frac{m}{M}\left[\gamma_{\bar{G}} - k_{\bar{G}}R^2 - (\gamma_G - k_G R^2)\right] (\hat{P}\cdot\hat{r})$$

$$+ K_G \frac{m}{M} (\gamma_{\bar{G}}^2 - \gamma_G^2) R \,. \tag{15}$$

The $L_{\pm G}$ in Eq. (14) are the conventional raising and lowering operators for the angular momentum operator

$$\vec{L}_G = -i\hbar \vec{\eta}_G \times \vec{\nabla}_{\eta_G} \,. \tag{16}$$

The quantity (Eq.(7)) in Eq. (14) is defined in Eq. (7) as indicated. At this stage the m/M differences between $\vec{R}, \vec{\xi}_{\bar{G}}$, and $\vec{\xi}_G$ can be neglected, and this will be done the next time the equations are rewritten. However the differences between γ_G and $\gamma_{\bar{G}}$ and $\vec{\eta}_G$ and

$\vec{r}_G$ are of order unity and are essential. In particular $\partial/\partial \vec{r}_G$ in Eq. (14) is taken with $\vec{r}_G$ fixed. The lower limit in Eq. (14) will be left undefined for the present. It is easy to get L^- from L^+. One reverses the signs of the superscripts on the C^* coefficients and takes the complex conjugate of everything else.

Equation (14) is very close to the Lagrangian which would result from a parametric, time-dependent formulation using a molecular basis and translational factors. The translational factors come from the first two terms of $\vec{r}_{GG'}$. To go to a time-dependent approximation one replaced all the K_G by a single $K_o(R)$ which relates R and time. The turning point for $K_o(R)$ is used as the lower limit on the integral over $\vec{r}_G$. The ultimate goal here however is to obtain a more refined semiclassical version of Eq. (14) using the Average *Approximation of* Riley.[4]

The dependence of Eq. (14) on the nuclear-reduced mass M is hard to assess because the nuclear center of mass has been used as an electron reference point. The internuclear midpoint is therefore introduced as a mass-independent reference point. Let $\vec{r}_m$ locate the electron with respect to this point. Then

$$\vec{r} = \vec{r}_m - (p-\tfrac{1}{2})\vec{R} \ , \qquad (17)$$

where $p = M_B/(M_A+M_B)$. From Eq. (11) the coordinate $\vec{r}_G$ is therefore related to $\vec{r}_m$ by

$$\vec{r}_G = \vec{r}_m + \gamma_{Gm}(R)\hat{R}, \tag{18}$$

where

$$\gamma_{Gm} = \gamma_G - (p-\tfrac{1}{2}),$$
$$\frac{d\gamma_{Gm}}{dR} = \frac{d\gamma_G}{dR}. \tag{19}$$

In Section III $\gamma_{Gm}(R)$ and k_G will be determined by varying L and found to be nearly independent of M. Thus $\vec{r}_G$ will be nearly independent of M. Consider Eq. (14) in the light of this information. First, simple manipulation of factors in Eq. (14) shows that up to order $\mathcal{E}_G/E$ M cancels out of Eq. (14) and Eq. (15) entirely except for the p-dependent terms. These will now be isolated in phase factors which help adjust the reduced mass of the separated fragments to their correct channel values to first order in m/M. From Eq (15)

$$\vec{r}_{GG} = \vec{r}_{cm} - K_G \frac{n}{M}\left[\gamma_{Gm} - k_G R^2 - (\gamma_{Gm} - k_G R^2)\right](p-\tfrac{1}{2})\,R$$
$$+ K_G \frac{m}{M}\,(\gamma_{\bar{G}}^2 - \gamma_G^2)R, \tag{20}$$

where the translational vector $\vec{\lambda}'$ is given by

$$\vec{\lambda}' = \frac{(K+\tfrac{1}{2})}{R}\,\frac{m}{M}\,(\gamma_{\bar{G}m} - \gamma_{\bar{G}\bar{m}})\,\hat{x}_m + K_{\bar{G}}\,\frac{m}{M}\left[\gamma_{\bar{G}m} - k_{\bar{G}}R^2 - (\gamma_{\bar{G}m} - k_{\bar{G}}R^2)\right]\hat{R}. \tag{21}$$

In writing Eqs. (20) and (21) the integration variables $\xi_{\bar{G}}$ have all been replaced by R and the state-dependent body fixed axes based on $\xi_{\bar{G}}$ and $\xi_{\bar{G}}$ have all been replaced by a set $\hat{x}_m$, $\hat{y}_m$, $\hat{z}_m = \hat{R}$ based on $\vec{R}$. This is permissible now since the consequent changes are of order m/M. The last two factors in Eq. (20) will next be removed. Let

$$C^{\pm}_{GG'} = e^{\mp\, iK_{\bar{G}}\frac{m}{M}R\left\{(p-\frac{1}{2})(\gamma_{\bar{G}m}-k_{\bar{G}}R^2) - \gamma_{\bar{G}}\right\}} D^{\pm}_{GG'},\quad R \geq T_{\bar{G}}$$

$$= D^{\pm}_{GG'},\quad R < T_{\bar{G}}. \tag{22}$$

When $C^{+}_{GG'}$ and $C^{-}_{G\bar{G}}$ are inserted in Eq. (14) and the differentiation carried out, the phase in Eq. (22) cancels the last two terms of $\Gamma_{\bar{G}\bar{G}}$ leaving just $\vec{\lambda}' \cdot \vec{r}_m$. In this cancellation, the small contribution of the difference between $K_{\bar{G}}$ and K_G was dropped. Now $D^{+}_{GG'}$ and $D^{-}_{G\bar{G}}$ appear in place of $C^{+}_{GG'}$, etc. The only other change is that the derivative of the phase from Eq. (22) has to be included with Eq. (7) in Eq. (14). The net result of this manipulation is

$$
\begin{aligned}
&\tfrac{1}{2}\{Lq.(7)\} + K_G \frac{d}{dR}\left(K_G \frac{m}{\hbar} R\left\{(p-\tfrac{1}{2})(\gamma_{Gm}-K_G R^2) - \gamma_G'\right\}\right) \\
&= \left(-\tfrac{1}{2}K_G' - \tfrac{1}{2}\frac{K(K+1)-\ell^2}{R^2}\right)\left(1 + \frac{m}{\hbar}(p-\tfrac{1}{2})^2\right) \\
&\quad + \tfrac{1}{2}\frac{2m}{\hbar^2}\left(E - \phi_G(R)\right) \\
&\quad - \frac{m}{2M}\left[\gamma_{Gm}^2 \frac{K(K+1)}{R^2} + K_G^2\,(\gamma_{Gm}-K_G R^2)^2\right] \qquad (23) \\
&\quad + \frac{m}{\hbar}\left(-RK_G\frac{K(K+1)}{R^2} + K_G^2\frac{d}{dR}(\gamma_{Gm}-K_G R^2)\right)(\vec{r}_m\cdot\hat{R}).
\end{aligned}
$$

In deriving Eq. (23) the approximate (free particle) relation

$$
\frac{dK_G}{dR} \cong \frac{K(K+1)}{K_G R^3} \qquad (24)
$$

was used to eliminate dK_G/dR. This is compatible with the value about to be chosen for K_G and consistent with the dropping of terms of order a_0^{-2} from Eq. (7). In Eq. (23) the large terms can be eliminated and the p-dependence joined with M by the choice $K_G^2 = (K_G')^2$, where

$$(\ell_G')^2 = \frac{2\mu'}{\hbar^2}\left(E - \epsilon_G(R) - \frac{K(K+1)-\ell^2}{R^2}\right)$$

$$\mu' = \mu / \left(1 + \frac{m}{M}(p-\tfrac{1}{2})^2\right) \quad . \tag{25}$$

With this choice of K_G', which shows that K_G' is insensitive to p, it is clear that the expression for L^+ in terms of D^+_{GG}, depends on M only through terms of order ϵ_G/E which must be fairly small if semiclassical analysis is to work at all. It would be possible to also eliminate the γ_{Gm} terms from Eq. (23) by adding $(m/M)\gamma_{Gm}$ to $(m/M)(P-\tfrac{1}{2})^2$ in Eq. (25). This produces a JWKB phase γ_G which together with the phase from Eq. (22) yields asymptotic radial scattering functions with the channel mass correct to first order in m/M.

Since $\frac{d\gamma_{Gm}}{dR}$ and $k_g R'$ approach zero as $R\to\infty$, the resulting equations also decouple. We prefer, however, to keep K_G' independent of the γ_{Gm}, to use the customary choice $K_G = \gamma_G'$, and to let the required phase develop in the function D^+_{GG}, through diagonal coupling terms. To recapitulate, in the expression (14) for L^+ replace the C's by D's from Eq.(22), replace γ_{GG} by $\bar{\gamma}+\gamma_m$ from Eq. (21) and replace $\tfrac{1}{2}$ Eq. (7)$_i$ by the right hand side of Eq. (23) with $K_G' = \ell_G'$ of Eq. (6).

The last step in the development of a semiclassical Lagrangian is to deal with the singularities in Eq. (14) arising from the $K_G^{-\frac{1}{2}}$ factors in the JWKB reference functions. Bates and Crothers[7] first showed that the straightforward retention of the factors $(K_G K_{\bar{G}})^{-\frac{1}{2}}$ in equations of the type of Eq. (14) was not a good approximation at low energy. They showed that much better results could be obtained by forcing a common turning point

for each pair of states $\bar{G}G$. Another successful approach to the problem is that of Gaussorgues et al.[ ] In this paper the Average Approximation of Riley[ ] will be used, although the other methods could also be adapted to the problems under consideration. In the average approximation, for $G \neq \bar{G}$, $(K_G K_{\bar{G}})^{\frac{1}{2}}$ and $\frac{1}{2}(K_G + K_{\bar{G}})$ are replaced by $K_{\bar{G}G}$, an average wave number defined by

$$K_{\bar{G}G} = (\frac{1}{2}(K_G^2 + K_{\bar{G}}^2))^{\frac{1}{2}}, \qquad \bar{G} \neq G , \tag{26a}$$

where

$$K_G^2 = \epsilon_G . \tag{26b}$$

As part of the same approximation the JWKB phase difference $\epsilon_G - \epsilon_{\bar{G}}$ is replaced by $\epsilon_{\bar{G}G}(R)$ with

$$\epsilon_{\bar{G}G}(R) = \int_{T_{\bar{G}G}}^{R} dx \frac{K_G^2 - K_{\bar{G}}^2}{2K_{\bar{G}G}} , \quad R \geq T_{\bar{G}G} . \tag{27}$$

In Eq. (27) the forced common turning point $T_{\bar{G}G}$ is the largest zero of $K_{\bar{G}G}$. Along with the above changes, the ratios $(K_G/K_{\bar{G}})^{\frac{1}{2}}$ will be set equal to 1, their high energy limit. This step appears to be essential because, by removing the singularities from the $id/d\epsilon_G$ terms, it paves the way for the discussion of unitarity given below.

At this point a generalization of Riley's method is required since in his application $T_{\bar{G}G}$ was identically zero. With $T_{\bar{G}G}$ equal to zero, the orthogonality of the electronic eigenfunctions makes the matrix of derivative terms (i.e., $dC^{+}_{\bar{G}G}/d\epsilon_{\bar{G}}$ terms) in Eq. (14) diagonal. Because he was dealing

with an orthonormal expansion, Riley was able to define the derivative term for all R. In the context of Eq. (14) this amounts to using the lower limit zero on the integral over the derivative terms. Riley's prescription for the off-diagonal coupling terms (i.e., the non-derivative terms in Eq (14)) is to exclude the $\bar{G}G$ coupling inside $T_{\bar{G}G}$. In Eq (14) this amounts to using the lower limit $T_{\bar{G}G}$ in the integrals over the coupling terms.

In the present case ($\ell_{\bar{G}G} \neq 0$) the same lower limits are adopted. Concurrently, $\vec{\chi}$ of Eq. (21) is replaced by $\vec{\chi}_{\bar{G}G}$, where

$$\vec{\chi}_{\bar{G}G} = \frac{(k+1)}{R}\frac{m}{M}(\ell_{\bar{G}m} - \ell_{Gm})\vec{x}_m + K_{\bar{G}G}\frac{m}{M}\left[\ell_{\bar{G}m} - k_{\bar{G}}R^{\ell} - (\ell_{Gm} - k_G R^{\ell})\right]\hat{R} \quad . \tag{28}$$

The above replacement of K_G by $K_{\bar{G}G}$ allows $\vec{\chi}_{\bar{G}G}$ to be defined for all $R \geq T_{\bar{G}G}$, so that all the coupling terms from Eq. (14) are defined. For $\ell_{\bar{G}G} \neq 0$, the non-diagonal derivative terms present a problem, since neither $\vec{\chi}_{\bar{G}G}$, nor $\ell_{\bar{G}G}$ of Eq.(27) are defined for $R < T_{\bar{G}G}$. A solution to this problem was found which is consistent with unitarity. By definition, with $dv = dx_m dy_m dz_m$, we take

$$\left[e^{i\vec{\chi}_{\bar{G}G}}\int dv \; e^{i\vec{\chi}_{\bar{G}G}\cdot\vec{r}_m}\,\vec{\chi}^{*}_{\bar{G}}\,\vec{\chi}_G\right](R) \tag{29}$$

$$= \left[e^{i\vec{\chi}_{\bar{G}G}}\int dv \; e^{i\vec{\chi}_{\bar{G}G}\cdot\vec{r}_m}\,\vec{\chi}^{*}_{\bar{G}}\,\vec{\chi}_G\right](T_{\bar{G}G}),\; R < T_{\bar{G}G} \quad .$$

For $R < T_{\bar{G}G}$, Eq. (29) fixes the $\bar{G}G$ overlap matrix, including $\Delta_{\bar{G}G}$, at the value it has at $R = T_{\bar{G}G}$. Forcing the constancy of the overlap matrix inside $T_{\bar{G}G}$ is

the unitary counterpart of dropping the coupling terms inside $T_{GG'}$, as will be shown presently. Let us first write down a new version of Eq. (14) which incorporates all the changes introduced thus far.

$$L^{+} = \frac{-\hbar^2}{M} \sum_{\vec{G}} \sum_{\vec{G}'} \left\{ \int_0^{\infty} dR D^{-}_{\vec{G}\vec{G}'}(R) i \mathscr{P}^{+}_{\vec{G}\vec{G}} \frac{dD^{+}_{\vec{G}\vec{G}'}}{dR}(R) \right.$$

$$\left. + \int_{T_{\vec{G}\vec{G}}}^{\infty} dR D^{-}_{\vec{G}\vec{G}'}(R)(-i) \mathscr{U}^{+}_{\vec{G}\vec{G}} D^{+}_{\vec{G}\vec{G}'}(R) \right\} \qquad (30)$$

where

$$\mathscr{P}^{+}_{\vec{G}\vec{G}}(R) = (-i)^{\lambda-\lambda'} e^{i\lambda_{\vec{G}\vec{G}}} \int dv\, e^{i\vec{\lambda}_{\vec{G}\vec{G}}\cdot\vec{r}_m} \chi^{*}_{\vec{G}} \chi_{\vec{G}}\,, \qquad (31)$$

and

$$-i\mathscr{U}^{+}_{\vec{G}\vec{G}}(R) = (-i)^{\lambda-\lambda'} e^{i\lambda_{\vec{G}\vec{G}}} \left\{ i \int dv e^{i\vec{\lambda}_{\vec{G}\vec{G}}\cdot\vec{r}_m} \chi^{*}_{\vec{G}} \left(\left(\frac{\partial}{\partial R}\right)_{\vec{r}_m} - (\gamma_{Gm} - k_G R^{-1}) \frac{\partial}{\partial z_m} \right) \chi_G \right.$$

$$+ \frac{(K+\frac{1}{2})(i)}{K_{\vec{G}\vec{G}} R^2} \int dv e^{i\vec{\lambda}_{\vec{G}\vec{G}}\cdot\vec{r}_m} \chi^{*}_{\vec{G}} \left(\frac{(-i)L_{y_m}}{\hbar} - R\gamma_{Gm} \frac{\partial}{\partial x_m} \right) \chi_G$$

$$\left. + \left[\frac{d}{dR} \left(\frac{m(k+\frac{1}{2})\gamma_{Gm}}{MR} \right) + \frac{(K+\frac{1}{2})}{K_{\vec{G}\vec{G}} R^2} \frac{m}{M} K_{\vec{G}\vec{G}} (\gamma_{Gm} - k_G R^{-1}) \right] \right.$$

$$\int dv\, e^{i\vec{K}_{\bar{G}}\cdot\vec{r}_m} \chi^*_{\bar{G}}(x_m, y_m, z_m)$$

$$+ \left[\frac{d}{dR}\left(\frac{m}{M} K_{\bar{G}\bar{G}} \left(\gamma_{Gm} - k_G R\right)\right) - \frac{(K+\frac{1}{2})}{K_{\bar{G}\bar{G}} R} - \frac{m}{M}\gamma_{Gm}\right]$$

$$\int dv\, e^{i\vec{K}_{\bar{G}}\cdot\vec{r}_m} \chi^*_{\bar{G}}(z_m)$$

$$- \left[\frac{1}{K_{\bar{G}\bar{G}}} \frac{m}{2M}\left(\frac{(K+\frac{1}{2})^2 \gamma_{Gm}}{R^2} + \left(K_{\bar{G}\bar{G}}(\gamma_{Gm} - k_G R)\right)\right)\right.$$

$$\left. + \frac{1}{K_{\bar{G}\bar{G}}} \frac{m}{2M} (p-\tfrac{1}{2})^2 \left(\frac{(K+\frac{1}{2})^2}{R^2} + K^2_{\bar{G}\bar{G}}\right)\right] \int dv\, e^{i\vec{K}_{\bar{G}\bar{G}}\cdot\vec{r}_m} \chi^*_{\bar{G}}(z_m) \Bigg| . \quad (32)$$

In arriving at Eq. (32) the $\chi_{\bar{G}}$ of Eq. (14) were all replaced by R and the matrix elements were expressed entirely in terms of the body-fixed mid-point variables x_m, y_m, z_m. The following additional modifications were also introduced in order that Eqs. (30)-(32) be exactly consistent with unitarity. First, all remaining K(K+1) factors were replaced by $(K+\frac{1}{2})^2$ so that $K+\frac{1}{2}$ appears everywhere. Second, in the third term of Eq. (23) K_G^2 was replaced by $K^2_{\bar{G}\bar{G}}$ to give the last term in Eq. (32). Finally, the coefficient of $\vec{r}_m\cdot\hat{R} = z_m$ was changed from its expression in Eq. (23) to the expression in the second-last term of Eq. (32). Taking into account the

general replacement of $P(P+1)$ by $(P+\frac{1}{2})^2$, the two expressions become equal when $d\mathscr{P}/dR$ is evaluated using the approximate Equation (24). The reason for these $d\mathscr{P}/dR$ changes is that to discuss unitarity one integrates the first term in Eq. (32) by parts. The quantities in Eq. (32) are such that terms arising from the derivative of $\mathscr{P}^+_{\bar{G}G}$ are compensated by terms from $\mathscr{W}^+_{\bar{G}G}$. More precisely,

$$\frac{d\mathscr{P}^+_{\bar{G}G}}{dR} + \mathscr{W}^+_{\bar{G}G} + \left(\mathscr{W}^+_{G\bar{G}}\right)^* = 0 \,, \tag{33}$$

$$\mathscr{P}^+_{\bar{G}G} = \left(\mathscr{P}^+_{G\bar{G}}\right)^* \,.$$

The coupling matrix element in Eq. (32) contains the as yet undefined quantities $K_{\bar{G}G}$. These appear because diagonal elements of the last two terms of Eq. (32) do not vanish identically as do the others. In Eqs. (14) and (23) $K_{\bar{G}G}$ is equal to K_G, the value given by Eq. (26a) if it is used for $\bar{G}=G$. Within the context of the approximations already made, the value of $K_{\bar{G}G}$ can be changed by amounts of order $\mathscr{P}_G/E$. So long as $K_{\bar{G}G}$ is real, its choice has no influence on unitarity. The choice $K_{\bar{G}G}=K_G$ is natural but has the drawback that, in addition to the off-diagonal turning points $T_{\bar{G}G}$, an additional set of diagonal ones is introduced. Another choice is

$$K_{\bar{G}G} \equiv K_{GK(G)} = \text{Any one of } \{K_{Gr};\ r \neq G\}$$

$$T_{\bar{G}G} \equiv T_{GK(G)} \tag{34}$$

In a two-state expansion one then has $T_{11} = T_{22} = T_{12}$. The use of Eq. (34) keeps the number of turning points in the formulation to a minimum. In the work of Riley, the diagonal coupling terms were eliminated through the choice of R_G^2. This approach was not used here in order to keep R_G independent of the parameters r_{Gm} and k_G. It should be emphasized that the use of Eq. (34) is a matter of convenience, not of principle.

The expression for $-i\hbar\dot{R}_{GG}^{+}$ given in Eq. (32) is based on the use of fixed nucleus electronic eigenfunctions for χ_G. It is convenient for some purposes to be able to use linear configurations of several electronic eigenfunctions to define each basis function χ_G. Let the electronic eigenfunctions be called ϕ_G in this paragraph and let

$$\chi_G = \sum_t U_{tG} \phi_t \tag{35}$$

where U is a real orthogonal matrix which connects only states of the same J. If χ_G is to be a "diabatic" state, U is chosen to reduce the adiabatic radial coupling amongst nearly crossing states to values of the same size as the adiabatic coupling away from the avoided crossings. The matrix U is also chosen so as to merely rename the adiabatic states in regions away from the crossings and to become diagonal in the separated atom limit. A more complete description of U is given in Section VI-B of I.[2]

With χ_G given by Eq. (35), Eq. (7) must be modified by the replacement of $F_G(r_G)$ by

$$F_G^D(r_G) = \langle \chi_G, H_e \chi_G \rangle \tag{36a}$$

in Eq. (8) and by the addition of the operator

$$\frac{-2\mu}{\hbar^2}\,(H_e - \mathcal{U}_G^0) \qquad (36b)$$

to [illegible] in Eq. (7). Here H_e is the fixed nucleus electronic Hamiltonian operator including the nuclear repulsion. The change in Eq. (7) is propagated into the last term of Eq. (14) and thence to Eq. (23) and finally to Eq. (32). With the understanding that Eq. (36a) is used to replace $\mathcal{U}_G$ in Eq. (8), the change in Eq. (32) required if χ_G is not an eigenfunction is the addition of the off-diagonal potential coupling,

$$-\frac{\hbar}{i^2 k_{GG}} \int dv\, e^{i\vec{\lambda}_{GG}\cdot\vec{r}_m}\, \chi_G^*\,(H_e - \mathcal{U}_{GG}^0)\chi_G \qquad (37)$$

to [illegible] in Eq. (32). With these changes Eq. (26)-(33) all hold. Of course, the parameters γ_{Gm}, and k_G are still associated with the χ_G, i.e., *with the diabatic states, not with the adiabatic eigenfunctions.* There is great flexibility possible in the choice of a transformation [illegible]. *"Mixed" representations are possible in which only selected groups of* adiabatic states are transformed, others being left unaltered. The primary interest in "diabatic" states here is that they offer a means of making γ_G and k_G more slowly varying functions of R.

Equations (30)-(33) are the final result. The incoming Lagrangian L^- is obtained from L^+ by reversing the signs of the superscripts of the

D's in Eq. (30) and taking the complex conjugate of everything else on the right-hand side. The whole Lagrangian L of Eq. (5) equals $L^+ + L^-$. To use Eq. (30) for variational purposes it is helpful to express $L^\pm$ as a sum of sub-Lagrangians; for example,

$$L^+ = \sum_{n=0}^{N} L_n^+ , \tag{31A}$$

such that the integrand in each L_n^+ is a differentiable function of R. Then for each n the usual manipulations of the calculus of variations are allowed. Following Riley,* let the distinct $T_{\bar{G}\bar{G}}$ be ordered according to increasing values $R_1, R_2, \cdots, R_N$ and let $R_0 = 0$ and $R_{N+1} = \infty$. The diagonal T_{GG} are to be included to the extent to which they are distinct. The R_i are called notch points. Let the sum of all terms in Eq. (30) for which the integration is over (R_n, R_{n+1}) define the sub-Lagrangian L_n^+, n=0,N. The formula for L_n^+ is

$$L_n^+ = -\frac{\pm^2}{M} \int_{R_n}^{R_{n+1}} dR \sum_{G} \sum_{\bar{G}} D^-_{\bar{G}\bar{G}'}(R)$$

$$\times \left\{ i\mathscr{V}^+_{\bar{G}\bar{G}} \frac{dD^+_{GG'}}{dR} + \delta(R_n - T_{\bar{G}\bar{G}})(-i)\mathscr{M}^+_{\bar{G}\bar{G}} D^+_{GG'}(R) \right\} . \tag{30}$$

The step function $\theta(x)$ has the value $\theta(x)=0$ for $x<0$, $\theta(x)=1$ for $x \geq 0$. The θ-function excludes from the sum in Eq. (39) all $\bar{G}\bar{G}$ combinations for which $T_{\bar{G}\bar{G}} > R_n$. By construction, if $T_{\bar{G}\bar{G}} > R_n$, $T_{\bar{G}\bar{G}} \geq R_{n+1}$, and for all R in (R_n, R_{n+1}), $R < T_{\bar{G}\bar{G}}$. Also, if $T_{\bar{G}\bar{G}} < R_n$, $T_{\bar{G}\bar{G}} < R$ for R in (R_n, R_{n+1}). This guarantees

the differentiability of the integrand in $\int_{R_n}^{R_{n+1}} dR$. In addition, from Eq. (29), it follows that, for $\bar{G} \neq G$, $\mathscr{S}_{G\bar{G}}(R) = \mathscr{S}_{\bar{G}\bar{G}}(T_{\bar{G}\bar{G}})$ in Eq. (39) if and only if the off-diagonal $\bar{G}G$ coupling term is excluded. The master equations for $D^+_{GG'}$ follow immediately by setting equal to zero the variation of L^- with respect to $D^-_{\bar{G}\bar{G}'}(R)$. The result for each n is that for $R_n < R < R_{n+1}$

$$\sum_G \left\{ i \mathscr{S}^+_{\bar{G}G} \frac{dD^+_{GG'}}{dR} + \theta(R_n - T_{\bar{G}G})(-i) \mathscr{M}^+_{\bar{G}G} D^+_{GG'} \right\} = 0 . \tag{40}$$

Note that a solution of Eq. (40) causes L^+_n to vanish for any set $\{D^-_{\bar{G}\bar{G}'}\}$. The equations for $D^-_{GG'}$ are given by Eq. (40) with $\mathscr{S}^+_{\bar{G}G}$ and $\mathscr{M}^+_{\bar{G}G}$ replaced by their complex conjugates. Beside Eqs. (33) the matrices $\mathscr{S}^+$ and $\mathscr{M}^+$ also satisfy

$$\mathscr{S}^+_{\bar{n},-\bar{\Lambda};n,-\Lambda}(R) = \mathscr{S}^+_{\bar{n},\bar{\Lambda};n,\Lambda}(R) ,$$

$$\mathscr{M}^+_{\bar{n},-\bar{\Lambda};n,-\Lambda}(R) = \mathscr{M}^+_{\bar{n},\bar{\Lambda};n,\Lambda}(R) . \tag{41}$$

As in Eq. (73)[2] these relations allow the equations to be partially diagonalized in the well-known way by introducing new even and odd variables, $2^{-\frac{1}{2}}(D^+_{n\Lambda} \pm D^+_{n-\Lambda})$ with $\Lambda > 0$, in place of $D^+_{n\Lambda}$, $D^+_{n-\Lambda}$. They also allow the tilde in Eq. (30) to be switched from one set of D's to the other.

It is now possible to apply the variational method to $L = L^+ + L^-$ of Eq. (5) and to discuss symmetry and unitarity. From Eq. (39) and the

corresponding expression for L^- the variation of L is given by

$$(L^+ + L^-) = \sum_n (-i\hbar^2 i/M) \int_{R_n}^{R_{n+1}} dR \sum_G \sum_{\bar{G}}$$

$$\cdot \Big\{ D^-_{\bar{G}G'} O^n_{GG} D^+_{GG'} - D^+_{\bar{G}G'} O^{n*}_{GG} D^-_{GG'}$$

$$+ D^-_{\bar{G}G'} O^n_{GG} D^+_{GG'} - D^+_{\bar{G}G'} O^{n*}_{GG} D^-_{GG'}$$

$$+ D^-_{\bar{G}G'} O^n_{GG} D^+_{GG'} - D^+_{\bar{G}G'} O^{n*}_{GG} D^-_{GG'} \Big\} , \qquad (42)$$

where

$$O^n_{GG} = \mathcal{N}^+_{GG} \frac{d}{dR} - (R_n - T_{GG}) \cdot \mathcal{N}^+_{GG} . \qquad (43)$$

The first term in each pair of terms in $\{\ \}$ of Eq. (42) comes from L^+, the second from L^-. The last pair of terms contains the variation with respect to the γ_G and k_G. We require that the $D^+_{GG'}$ satisfy the outgoing Eq. (40) and that the $D^-_{GG'}$ satisfy the incoming equation,

$$\sum_G O^{n*}_{GG} D^-_{GG'} = 0 . \qquad (44)$$

Thus, the first pair of terms vanishes. The second pair of terms is treated by integration by parts using Eq. (33), continuity, and the connection equations (4).

The short calculation shows that

$$\sum_n (-\hbar^2 i/M)\int_{R_n}^{R_{n+1}} dR \sum_{\bar{G}} \sum_{G} \left\{ D^-_{\bar{G}G} O^n_{GG} \partial D^+_{GG'} - D^+_{\bar{G}G'} O^{n*}_{GG} \partial D^-_{GG'} \right\}$$

$$= \sum_n (-\hbar^2 i/M)\int_{R_n}^{R_{n+1}} dR \sum_{\bar{G}} \sum_{G} \left\{ \partial D^-_{GG'} O^n_{GG} D^+_{GG'} - \partial D^+_{GG'} O^{n*}_{GG} D^-_{GG'} \right\}$$

$$-(\hbar^2 i/M) \sum_{n,G} \left(D^-_{n-1,\bar{G}'}(\infty) \partial D^+_{n-1,G'}(\infty) - D^+_{n-1,\bar{G}'}(\infty) \partial D^-_{n-1,G'}(\infty) \right) . \qquad (45)$$

Thanks to Eqs. (41), the first term on the right hand side of Eq. (45) vanishes if, as we require, the functions $D^{\pm}_{GG'}$ also satisfy Eqs. (40) or (44). The second term on the right hand side of Eq. (45) produces the variation of the scattering amplitude for transitions between states $\bar{G}'$ and G' as required by the variational principle.[10] Thus the final result of using the variational principle with Eqs. (40) and (44) is that the last pair of terms in Eq. (42) must vanish. That is,

$$\sum_n (-\hbar^2 i/M)\int_{R_n}^{R_{n+1}} dR \sum_{G\bar{G}} \left(D^-_{\bar{G}G} \partial O^n_{GG} D^+_{GG'} - D^+_{\bar{G}G'} \partial O^{n*}_{GG} D^-_{GG'} \right) = 0 . \qquad (46)$$

This equation is the basis for the developments in Section III. In Eq. (45), the ∂ can be omitted. In this form the left hand side of Eq. (45) is equal to $L = L^+ + L^-$, while the first term on the right hand side is L with the roles of the two trial solutions exchanged. Both terms vanish for solutions of Eqs. (40) and (44). The last term of Eq. (45) must therefore vanish leading to a relation between asymptotic values of the D's. It should be straightforward to prove unitarity and detailed balance from these equations, using the equations starting with Eq. (75)[2] to relate the $D^+_{GG'}(\infty)$ to the components of the S-matrix.[11]

We conclude this section by briefly returning to the master equation (40). A little study of $\mathscr{V}^{+}_{GG}$ and $\mathscr{W}^{+}_{GG}$ in Eqs. (31) and (32) shows that they resemble closely equations from earlier work, particularly if a single trajectory approach is introduced and if, for example, constant Bates-McCarroll translational factors are used. The added complexity arises from the use of R-dependent translation factors and from the semi-classical Average Approximation. Some of the terms in $\mathscr{W}^{+}_{GG}$ are of order $mva_0/\hbar$ compared to the main coupling terms. They may not be very important in some cases, but their neglect will make the first of Eqs. (33) inexact.

III. SEMICLASSICAL VARIATIONAL DETERMINATION OF THE TRANSLATIONAL FACTORS

Equations (30)-(32) contain the undetermined functions $\gamma_{Gm}(R)$ and $k_G(R)$ for each term G in the scattering expansion. The basic tool for their evaluation is Eq. (46). It can be seen from Eqs. (28)-(32) and Eq. (43) that in Eq. (46) the quantity $\gamma_{Gm}-k_G R^2$ appears as a unit. Therefore let

$$u_{Gm} = \gamma_{Gm} - k_G R^2 \tag{47}$$

Then Eq. (46) contains u_{Gm}, $\dot{u}_{Gm}$, γ_{Gm}, and $\dot{\gamma}_{Gm}$ and the variation (46) leads to standard Euler-Lagrange equations. Here the dot signifies the derivative with respect to R. Let the symbol w_G represent the abstract vector with components (u_{Gm}, γ_{Gm}) so that one equation in w_G stands for a pair of equations, one for u_{Gm} and one for γ_{Gm}. The Euler-Lagrange equations from Eq. (46) are

$$\sum_{\bar{G}}\sum_{G} D^{-}_{\bar{G}G}, \frac{\partial O^{n}_{GG}}{\partial w_H} D^{+}_{GG'} - \frac{d}{dR}\sum_{\bar{G}}\sum_{G} D^{-}_{\bar{G}G}, \frac{\partial \dot{O}^{n}_{GG}}{\partial w_H} D^{+}_{GG'}$$

$$-\sum_{\bar{G}}\sum_{G} D^{+}_{\bar{G}G}, \frac{\partial O^{n*}_{GG}}{\partial w_H} D^{-}_{GG'} + \frac{d}{dR}\sum_{\bar{G}}\sum_{G} D^{+}_{\bar{G}G}, \frac{\partial \dot{O}^{n*}_{GG}}{\partial w_H} D^{-}_{GG'} = 0 , \tag{48}$$

where O^{n}_{GG} is defined by Eq. (43). In Eq. (43) $\mathcal{P}^{+}_{GG}$ is constant whenever $\delta(R_n - T_{GG})$ is zero and in this circumstance its contribution to Eq. (48) is zero. From Eqs. (31), (32), (28), and (8)

$$\frac{\partial \mathcal{W}^{\dagger}_{GG}}{\partial w_H} = 0 \ , \qquad \frac{\partial}{\partial w_H}\frac{d\mathcal{W}^{\dagger}_{GG}}{dR} = \frac{d}{dR}\frac{\partial \mathcal{W}^{\dagger}_{GG}}{\partial w_H} \ ,$$

$$\frac{\partial}{\partial k_H}\frac{d\mathcal{W}^{\dagger}_{GG}}{dR} = \frac{\partial \mathcal{W}^{\dagger}_{GG}}{\partial w_H} \ ,$$

$$\frac{\partial}{\partial \dot{u}_{Hm}} \mathcal{W}^{\dagger}_{GG} = i\,\frac{m}{M}\,K_{GG}\,(z_m)_{GG}\,\delta_{GH} \ ,$$

$$\frac{\partial}{\partial \dot{r}_{Hm}} \mathcal{W}^{\dagger}_{GG} = i\,\frac{m}{M}\,\frac{(K+\tfrac{1}{2})}{R}\,(x_m)_{GG}\,\delta_{GH} \ , \tag{49}$$

where

$$(\vec{r}_m)_{GG} = (-i)^{\frac{1}{2}-\frac{1}{2}} e^{i\vec{k}_{GG}} \int dv\, e^{i\vec{k}_{GG}\cdot\vec{r}_m}\, \chi^{*}_{G}\, \vec{r}_m\, \chi_G \ . \tag{50}$$

Finally, from Eq. (32),

$$\frac{\partial \mathcal{W}^{\dagger}_{GG}}{\partial r_{Hm}} = \frac{(K+\tfrac{1}{2})}{K_{GG}R}\left(\frac{\partial}{\partial x_m}\right)_{GG}\delta_{GH} - i\,\frac{m}{M}\,\frac{(K+\tfrac{1}{2})}{R^2}\,(x_m)_{GG}\,\delta_{GH}$$

$$-i\,\frac{(K+\tfrac{1}{2})}{K_{GG}R^3}\,\frac{m}{M}\,(z_m)_{GG}\,\delta_{GH} - \frac{i}{K_{GG}}\,\frac{m}{M}\,\frac{(K+\tfrac{1}{2})^2}{R^2}\,\gamma_{Hm}\,\mathcal{P}_{GG}\,\delta_{GH}$$

$$+i\,\frac{(K+\tfrac{1}{2})}{R}\,\frac{m}{M}\,(\delta_{GH} - \delta_{GH})\,Q_{xGG} \ , \tag{51}$$

$$\frac{\partial \mathscr{M}^{+}_{\bar{G}G}}{\partial u_{Hm}} = \left(\frac{\partial}{\partial z_m}\right)_{\bar{G}G} \delta_{GH} + i\,\frac{(K+k)}{P^2}\,\frac{m}{M}\,(x_m)_{\bar{G}G}\,\delta_{GH} + i\,\frac{d}{dR}\left(\frac{m}{M}\,K_{\bar{G}G}\right)(z_\pi)_{\bar{G}G}\,\delta_{GH}$$

$$-i\,\frac{m}{M}\,K_{\bar{G}G}\,u_{Hm}\,\mathscr{M}^{+}_{\bar{G}G}\,\delta_{GH} + i\,K_{\bar{G}G}\,\frac{m}{M}\,(\delta_{GH} - \delta_{GH})\,Q_{z\bar{G}G} \quad . \qquad (52)$$

In Eqs. (51) and (52) the gradient matrix elements are defined in the same way $(\vec{r}_m)_{\bar{G}G}$ is defined by Eq. (50). The matrix element $Q_{x\bar{G}G}$ is obtained by inserting an x_m next to $\exp(i\vec{\lambda}_{\bar{G}G}\cdot\vec{r}_m)$ in each integral in the expression (32) for $\mathscr{M}^{+}_{GG}$; $Q_{z\bar{G}G}$ is defined analogously. The derivatives $dD^{\pm}_{GG'}/dR$ can be eliminated from Eq. (48) using Eqs. (40) and (44). Eq. (48) can then be written in the form

$$\sum_{\bar{G}}\sum_{G}\left\{D^{-}_{\bar{G}\bar{G}},\ \Gamma^{H}_{\bar{G}G}\,D^{+}_{GG'} - D^{+}_{\bar{G}\bar{G}}\,\Gamma^{H*}_{\bar{G}G}\,D^{-}_{GG'}\right\} = 0 \quad . \qquad (53)$$

Eq. (53) holds for each H, and each component of w_H in $\Gamma^{H}_{\bar{G}G}$. In matrix notation, omitting the matrix subscripts,

$$\Gamma^{H} = -\frac{\partial \mathscr{P}^{+}}{\partial w_H}\,(\mathscr{P}^{+})^{-1}\,\mathscr{M}^{+} + \frac{\partial \mathscr{M}^{+}}{\partial w_H} - \frac{d}{dR}\,\frac{\partial \mathscr{M}^{+}}{\partial \dot{w}_H}$$

$$-\frac{\partial \mathscr{M}^{+}}{\partial \dot{w}_H}\,(\mathscr{P}^{+})^{-1}\,\dot{\mathscr{M}}^{+} - \dot{\mathscr{M}}^{+\dagger}\,(\mathscr{P}^{+})^{-1\dagger}\frac{\partial \mathscr{M}^{+}}{\partial w_H} \quad . \qquad (54)$$

Another version is

$$\Gamma^{H} = \frac{\partial \mathscr{M}^{+}}{\partial w_H} - \frac{d}{dR}\,\frac{\partial \mathscr{M}^{+}}{\partial \dot{w}_H} + \frac{\partial \dot{\mathscr{M}}^{+\dagger}}{\partial \dot{w}_H}\,(\mathscr{P}^{+})^{-1}\,\mathscr{M}^{+} - \mathscr{M}^{+\dagger}\,(\mathscr{P}^{+})^{-1\dagger}\frac{\partial \mathscr{M}^{+}}{\partial \dot{w}_H} \quad . \qquad (55)$$

In Eqs. (54) and (55), $\mathscr{H}^{+}_{\bar{G}G} = (R_n - T_{\bar{G}G})\mathscr{H}^{+}_{\bar{G}G}$ and + signifies the complex conjugate of the transpose. Eq. (55) was obtained using Eqs. (33) and (49). The same equations can be used to show that $\mathscr{T}^{H}$ is antiHermitian.

Equations (53), (40), and (44) are supposed to be solved simultaneously. Therefore, the optimization of the parameters γ_{Gm} and u_{Gm} leads to an enlarged set of first order coupled equations in which γ_{Hm}, u_{Hm} and the $D^{\pm}_{GG'}$ are to be determined simultaneously. Moreover, the equations are complicated by the presence of w_H in $\mathscr{T}_{\bar{G}G}$ and this brings w_H into the matrix elements in Eqs. (31) and (32) in a rather awkward way.

It was to be expected on general grounds and from the work of Riley & Green that the determination of the $D^{\pm}_{GG'}$ is coupled with that of w_H. In that work[5] the same problem under discussion here was approached from the standpoint of time-dependent theory. To make contact with that formulation one only has to replace all the $K_{\bar{G}\bar{G}}$ by a single local wave number $K_0(R)$ with $K_0(R_1)=0$. The only intervals (Section II) are $(0,R_1)$ and (R_1,∞). Then the equations $dt = \pm MdR/(\hbar K_0)$ and $t(R_1)=0$ relate the time and the radial velocity in the classical way. Reference 5 discussed the optimization of expansions containing translational factors of several forms, and in particular solved the present optimization problem for a one-state expansion.

In this case we should optimize with $G=\bar{G}=G'=\bar{G}'$ and, because $\mathscr{T}^{H}_{GG}$ is imaginary, Eq. (53) reduces to $\mathscr{T}^{G}_{GG}=0$. Also $\vec{\lambda}_{GG}=\vec{0}$ and the only diagonal terms in $\mathscr{H}^{+}_{GG}$ are proportional to $(z_m)_{GG}$ and $\mathscr{S}^{+}_{GG}=1$. From Eq. (53) one obtains the simple but important one-state results

$$\gamma_{Gm} = -(z_m)_{GG}/R \ ,$$

$$u_{Gm} \quad \gamma_{Gm} - k_G R^2 = -\frac{d}{dR}(z_m)_{GG} \ ,$$

$$k_G = -\frac{1}{R}\frac{d\gamma_{Gm}}{dR} \ . \tag{56}$$

Now $(z_m)_{GG}$ determines the center of electronic charge for the state G, measured from the midpoint of the internuclear line. Equations (56) are equivalent to Eq. (16) of Ref. 5. As $R \to \infty$, $(z_m)_{GG} \to \epsilon_G R/2$ where ϵ_G is minus one for states correlating to states on nucleus A and plus one otherwise. Thus as R

$$k_G R^2 \to 0$$

$$\gamma_{Gm} \to -\tfrac{1}{2}\epsilon_G \ . \tag{57}$$

As Bates and McCarroll first showed,[3] this is precisely the behavior required to make the radial coupling matrix element vanish in Eq. (32) and to make the angular coupling matrix element tend toward a constant.[12]

Thus, as Ref. 5 established, the one-state optimization yields translational factors (56) in which the scattering equations decouple in the separated atom limit. In the united atom limit $(z_m)_{GG}$ approaches $(-\tfrac{1}{2}+z_B/(Z_A+Z_B))R$ for any state G which is the lowest in energy of its symmetry class. Then

$$\gamma_{Gm} \cdot \gamma - z_B/(z_A + z_B)$$

$$\gamma_{Gm} - k_G R \cdot \gamma - z_B/(z_A + z_B) \quad . \tag{58}$$

If z_A and z_B are not very different, γ_{Gm} is small; if one of the charges is large compared to the other, γ_{Gm} is close to the separated-atom value for the large charge. Equations (53) are not generally compatible with Eqs. (46),[2] which require that as $R \to 0$,

$$\gamma_G R^{-1} = (\gamma_{Gm} + M_B/(M_A + M_B) - \tfrac{1}{2})R^{-1} \to 0 \ ,$$

$$k_G \to 0 \ . \tag{59}$$

In writing Eq. (59), Eq. (19) was used. Conditions (59) were introduced so that as $R \to 0$ the reaction coordinate $\vec{r}_G$ would tend toward the internuclear separation $\vec{R}$ fast enough to keep the angle between $\vec{r}_G$ and $\vec{R}$ of order m/M for all R. From Eqs. (56) and (59), it is seen that $\gamma_{Gm}+M_B/(M_A+M_B) - \frac{1}{2}$ will vanish exactly only when the center of mass of the nuclei coincides with the center of charge. The rule nuclear mass $\sim$ 2 times nuclear charge does indeed tend to keep the difference between the two centers small. In order to satisfy Eq. (59) it will be assumed that in the region $(0,R_1)$, where R is inside all the turning points, γ_G and k_G are extrapolated to the origin in such a way as to satisfy Eq. (59). Since we are concerned with a theory of slow collisions, there is a lower bound on R_1. The important restriction in any event is to keep the angle between $\vec{r}_G$ and $\vec{R}$ very small since this assumption was used to simplify the scattering equations. If the solution of Eqs. (53) should happen to violate this condition at small R, the solution should be modified appropriately.

(The use of less than optimal translational factors is not as dangerous as violating the assumptions used to derive the scattering equations.) When two or more states of the same symmetry are degenerate at R=0, Eqs. (58) may not hold. However it is still necessary to make sure that Eq. (59) is not violated.

It is significant that the one-state optimization does not yield the p.s.s. coordinate choice, $\gamma_G=k_G=0$, and yields the Bates-McCarroll result only as $R\to\infty$.

Let us now return to the many-channel equations (53) and ask if the one-state solution (56) also satisfies the multistate equations (53) in the separated-atom limit. A straightforward but somewhat tedious calculation shows that in this limit $\mathcal{P}^+_{GG}$ and $\mathcal{W}^+_{GG}$ become diagonal and that for the solution (56), as $R\to\infty$, Γ^H of Eq. (55) takes the form

$$\Gamma^H_{GG} \to \tfrac{1}{4}\frac{\pi}{M}\left(k_G + (p-\tfrac{1}{2})^2\right)\left(\frac{z_m}{\gamma_m}\right)_{GG}\left(\gamma_{GH} + \gamma_{GH}\right) \tag{60}$$

for the u_{Gm} component of w_G. The component of Γ^H, Eq. (55), corresponding to γ_G tends toward zero. The right hand side of Eq. (60) is $O(m/Ma_0)$ while the terms which were set equal to zero to deduce Eqs. (56) are of order (mK_{GG}/M), as can be seen from Eq. (63). Thus as $R\to\infty$ the one-state solutions also satisfy the multistate equations (53) to relative order $1/K_{GG}a_0 \to 1$.

Since the one-state solutions (56) appear to have reasonable properties it is tempting to use them directly in connection with Eq. (40) and avoid any further complications. This approach works for isolated states. However, when two states undergo an avoided crossing, the centers of electronic charge $(z_m)_{GG}$ for the two states may change

very rapidly and non-monotonically with internuclear separation in the vicinity of the avoided crossing. This can lead to large, abrupt, non-monotonic changes in the value of v_{Gm} given by Eq. (56) and corresponding numerically undesirable variations in $\dot{v}_{Gm}$ in Eq. (32). In addition, in some applications to homopolar systems, where gerade and ungerade states may be combined, the quantity corresponding to $(z_m)_{GG}$ in Eq. (56) may remain finite as $R \to 0$, causing a troublesome singularity.[5] For these reasons, it is worth seeking a generalization of the one-state formulae in the hope of finding more smoothly varying solutions.

Consider the diagonal elements Γ^H_{GG} of Eq. (55). Because of the appearance of ζ_{GH} in Eq. (49)

$$\Gamma^H_{GG} = \Gamma^G_{GG}\,\zeta_{GH} \quad . \tag{61}$$

Also, Γ^H_{GG} is imaginary.

Therefore by setting Γ^G_{GG} equal to zero for each G, the diagonal terms of the sum in Eq. (53) can be made to vanish for all H. Thus, if the off-diagonal terms in Eq. (53) are small, the equation

$$\Gamma^G_{GG} = 0 \quad , \tag{62}$$

is a good substitute for Eqs. (53). At sufficiently low velocities Eq. (62) should certainly be a good approximation when the expansion is based on adiabatic molecular states; for then, because the coupling is weak, the factors in the off-diagonal terms are small. At higher

velocities, where the avoided crossings of the system are behaving diabatically, but the coupling away from avoided crossings is still weak, linear combinations of the nearly-crossing adiabatic states can be formed into "diabatic states" for which the "diabatic" coupling is weak everywhere. Then Eq. (62) should again be a good approximation to Eq. (53). In this case Eq. (40) has to be modified as described in Section II to account for the use of the diabatic states in the expansion. The result of using Eq. (62) for systems with avoided crossings is that away from the avoided crossings adiabatic and diabatic formulations yield the same translational factors. As the crossings are traversed, the diabatic factors change very little while the multistate adiabatic ones switch monotonically as the adiabatic state changes its character.

Another approach to Eqs. (53) was outlined in the Introduction to Ref. 2. We postulate that the parameters γ_G and ω_G are to be slowly varying functions compared to the oscillating factors in Eq. (46) and place this restriction on its solution. How best to do this is not clear to the author, but perhaps one way is to average Eq. (53) over the R-dependent oscillations in the products, $D^-_{G\bar{G}'} D^+_{GG'}$. This should annihilate the off-diagonal terms in Eq. (53), except around avoided crossings. This approach has not been explored further.

The difference between adiabatic and diabatic translational factors near avoided crossings may not be very important. Whenever $\gamma_{\bar{G}} - \gamma_G$ is very small, $(\partial/\partial \vec{R}_m)_{\bar{G}G}$ is very small. Thus in Eq. (32), the influence of the translational factors on the radial and angular coupling should be minimal. This suggests that even in the strong-coupling case when a given avoided crossing is behaving neither adiabatically nor diabatically but the coupling

is weak away from avoided crossings, both formulations can be applied successfully. This conjecture remains to be tested.

An important advantage of Eq. (62) is that the calculation of v_{Gm} and u_{Gm} has been split off from Eq. (40). The mutually coupled equations (63) and (40) are certain to yield functions $v_{Gm}(R)$ which are modulated by the characteristic spatial frequencies in $\tilde{v}_{GG}$ of Eqs. (31) and (32). This hardly seems desirable. From Eqs. (62) and (55), for each G,

$$-i\frac{m}{M}\frac{(K+k)^2}{K_{GG}R^2}\left(\frac{}{v_{Gm}}+\frac{(z_m)_{GG}}{R}\right)\theta(R_n-T_{GG})$$

$$+2i\ \mathrm{Im}\left\{\sum_r\sum_s -i\frac{m}{M}\frac{(K+k)}{R}(x_m)_{Gr}(\mathscr{S}^+)^{-1}_{rs}\ \mathscr{U}^+_{sG}\,\theta(R_n-T_{Gr})\ \theta(R_n-T_{Gs})\right\}$$

$$=0\ , \qquad (63a)$$

$$-i\frac{m}{M}K_{GG}\left(u_{Gm}+\frac{d}{dR}(z_m)_{GG}\right)\theta(R_n-T_{GG})$$

$$+2i\ \mathrm{Im}\left\{\sum_r\sum_s -i\frac{m}{M}K_{Gr}(z_m)_{Gr}(\mathscr{S}^+)^{-1}_{rs}\ \mathscr{U}^+_{sG}\,\theta(R_n-T_{Gr})\ \theta(R_n-T_{Gs})\right\}$$

$$=0\ . \qquad (63b)$$

In Eqs. (63) $\mathscr{S}^+$ and $\mathscr{U}^+$ are defined by Eqs. (31) and (32) while (x_m) and (z_m) are defined by Eq. (50). The symbol Im ( ) means the imaginary part of ( ). The equations apply to the interval (R_n,R_{n+1}) of Section II.

Eqs. (63) exhibit a problem. The K_{Gr} and their reciprocals are contained in Eqs. (63) both explicitly and through $\mathscr{U}^+_{sG}$. Therefore,

any time $R_n = T_{Gr}$ or $R_n = T_{Gs}$ in Eqs. (63) some term can become zero or singular for $R = R_n$. Outside all the turning points, where the K_{Gr} are equal to order ϵ_G/E, the equations are well behaved. It is seen that Eqs. (63) can cause τ_{Gm} and u_{Gm} to depend substantially on the K_{Gr} of the Average Approximation. However, the original derivation of the semiclassical Lagrangian (30), was based on the neglect of various terms of order ϵ_G/E compared to 1, for example in setting $(K_G/K_r)^{\frac{1}{2}}$ equal to unity. From the way τ_{Gm} and u_{Gm} appear in Eqs. (28), (31) and (32), it is clear that changes of order ϵ_G/E in these quantities are of the same order as the changes from K_G to $K_{\bar{G}}$ or to $K_{\bar{G}\bar{G}}$ which were neglected in the derivation of the Lagrangian. Therefore the Lagrangian cannot be used to infer information about τ_{Gm} and u_{Gm} beyond the level of accuracy in which all the K_{rG} are set equal to one another, along with their turning points T_{rG}. In the decoupled approximation (63) this is possible without simultaneously going over to a one-trajectory version of Eq. (40). Thus in Eqs. (63) we set

$$K_{Gr}(R) = K_0(R)$$

$$T_{Gr} = T_0 \tag{64}$$

with T_0 chosen for convenience to be the smallest of all $T_{\bar{G}\bar{G}}$, i.e., $T_0 = R_1$, and K_0 chosen to be the corresponding $K_{\bar{G}\bar{G}}$. Then for all intervals $(R_{n,n+1})$, $n \geq 1$, the η functions in Eqs. (58) are unity and the K_{Gr} are all set equal to $K_0(R)$. This same result could have been obtained directly from an initial common-trajectory approach such as the time-dependent impact parameter method[5] or the semiclassical method of Gaussorgnes et al.[6] Thanks to the use of a common trajectory, $\Delta_{\bar{G}\bar{G}}$ of Eqs. (31), (32), and (50) becomes a difference of the form

$Q_G - Q_{\bar{G}}$ and $(i)^{\vec{\lambda}_{GG}} \exp(i\vec{\lambda}_{GG})$ in the several matrix elements can be dropped in the evaluation of Eqs. (63). Finally, $\vec{\lambda}_{GG}$ in Eqs. (28), (31), (32), and (50) becomes a difference

$$\vec{\lambda}_{GG} = \vec{\lambda}_{\bar{G}} - \vec{\lambda}_G \quad ,$$

$$\vec{\lambda}_G = \frac{K + \frac{1}{2}}{R} \frac{m}{M} r_{Gm} \hat{x}_m + K_0 \frac{m}{M} u_{Gm} \hat{z}_m \quad . \tag{65}$$

Note that Eq. (65) is only going to be used in connection with Eqs. (63), not with Eqs. (40), for which the Average Approximation can be retained.

Let us now rewrite Eqs. (63) to reflect the foregoing simplifications. We find

$$r_{Gm} + \frac{(z_m)_{GG}}{R} + 2 \frac{K_0 R}{(K + \frac{1}{2})} \operatorname{Im} \left\{ \sum_r \sum_s i(x_m)_{Gr} \mathscr{A}^{-1}_{rs} \mathscr{A}^{+}_{sG} \right\} = 0 \quad , \tag{66a}$$

$$u_{Gm} + \frac{d}{dR} (z_m)_{GG} + 2 \operatorname{Im} \left\{ \sum_r \sum_s i(z_m)_{Gr} \mathscr{A}^{-1}_{rs} \mathscr{A}^{+}_{sG} \right\} = 0 \quad , \tag{66b}$$

where

$$\mathcal{H}^{+}_{sG} = -\left(\frac{\partial}{\partial R}\right)_{r_m}{}_{sG} + \left(\frac{\partial}{\partial z_m}\right)_{sG} u_{Gm} - \frac{(K+\frac{1}{2})}{k_0 R^2}\left(\frac{-iL_m}{\hbar}\right)_{sG}$$

$$+\frac{(K+\frac{1}{2})}{k_0 R}\left(\frac{\partial}{\partial z_m}\right)_{sG} \gamma_{Gm} - i\frac{M}{\hbar^2 k_0}\left[(H_e)_{sG} - \mathcal{E}^{D}_{GG}\mathcal{S}^{+}_{sG}\right]$$

$$-i\frac{m}{M}\frac{(K+\frac{1}{2})}{R^2}(x_m)_{sG}\, k_G R^2 - i\frac{m}{M}\frac{(K+\frac{1}{2})^2}{k_0 R^2}\frac{(z_m)_{sG}}{R}\, k_G R^2$$

$$+i\frac{m}{M}\frac{(K+\frac{1}{2})}{R}(x_m)_{sG}\frac{d\gamma_{Gm}}{dR} + i\frac{m}{M}k_0 (z_m)_{sG}\frac{du_{Gm}}{dR} - i\,\mathcal{S}^{+}_{sG}[\,]. \quad (67)$$

Eq. (67) was obtained from Eq. (32). The matrix elements in Eq. (67) are defined the same way $(\vec{r}_m)_{\bar{G}G}$ is defined in Eq. (50). However the $(-1)^{\bar{l}-l}\exp i\zeta_{GG}$ can be dropped everywhere, and Eq. (65) is to be used for $\bar{\gamma}_{GG}$ in all matrix elements. The term $k_G R^2$ can be replaced by $\gamma_{Gm}-u_{Gm}$ according to Eq. (47). In obtaining Eq. (67) from Eq. (32) Eq. (24) was used to evaluate dK_0/dR. The [ ] in Eq. (67), which is real, is not needed because the contribution of the $-i\mathcal{S}^{+}_{sG}[\,]$ term to $\{\,\}$ in Eqs. (66) is real. Equation (37) was used to allow for the use of some "diabatic states."

We now discuss the properties and solution of Eqs. (66). The first noteworthy point is that when the sums in Eqs. (66) are carried out over a complete set of states, the multistate term cancels the one-state terms. In this property only the first four terms of $\mathcal{H}^{+}_{sG}$ are effective; the others all contribute real quantities to $\{\,\}$ in Eqs. (66). Although a complete set is never contemplated in this work, it is clear that the multistate

terms are taking something away from the one-state parts of Eqs. (66). It turns out that this is what smooths out the multistate adiabatic translational factors in the vicinity of avoided crossings relative to the single-state adiabatic result.

Because $\omega_{Sm}-\omega_{Gm}$ and $u_{Sm}-u_{Gm}$ appear in $\mathcal{H}^{+}_{SG}$, the solutions of the non-linear first-order differential equations (66) are not easy to study in general. At low velocities such that $(mva_0/\hbar)^2$ can be neglected compared to unity, all the (m/M) terms can be dropped from $\mathcal{H}^{+}_{SG}$ in Eq. (67) compared to the first five terms. In the matrix elements of the first four terms $\exp i\vec{\kappa}_{GG}\cdot\vec{r}_m$ can be set equal to unity and in the fifth term it can be set equal to $1+i\vec{\kappa}_{GG}\cdot\vec{r}_m$. In this approximation the first two terms of $\mathcal{H}^{+}_{SG}$ contribute only to Eq. (66b), and the second two contribute only to Eq. (66a). The diabatic term (i.e. the fifth one) is more complex. In the expansion of $\exp i\vec{\kappa}_{GG}$ in the three matrix element product in $\langle\ \rangle$ of Eqs. (66), unity is used in two matrix elements and $i\vec{\kappa}_{GG}\cdot\vec{r}_m$ is used in the third. The result is that Eqs. (66) become coupled linear equations; the λ_{Gm} are not coupled with the u_{Gm}, however. Also, the common trajectory parameters factor out completely. The low-velocity result can be written

$$\left(1 + 2\sum_r \langle x_m\rangle_{Gr}\left\langle\frac{\partial}{\partial x_m}\right\rangle_{rG}\right)\gamma_{Gm} + \frac{\langle z_m\rangle_{GG}}{R}$$

$$- \frac{2}{R}\sum_r \langle x_m\rangle_{Gr}\left\langle\frac{i}{\hbar}L_{y_m/rG}\right\rangle + \text{diabatic terms in } \gamma_{Hm} = 0\ , \qquad (68a)$$

$$\left(1 + 2\sum_r \langle z_m\rangle_{Gr} \left\langle \frac{\partial}{\partial z_m}\right\rangle_{rG}\right) u_{Gm} + \frac{d}{dR}\langle z_m\rangle_{rG}$$

$$-2\sum_r \langle z_m\rangle_{Gr} \left\langle \left(\frac{\partial}{\partial R}\right)_{r_m}\right\rangle_{rG} + \text{diabatic terms in } u_{Gm} = 0 \,. \qquad (68b)$$

In Eqs. (68) $\langle\ \rangle$ denotes a conventional matrix element between fixed-nucleus electronic basis functions. The diabatic terms come from the fifth term of Eq. (67), evaluated as described above. They do not contain P^{+1} or P_0 and are all of order $ma_0/\hbar$ times the off-diagonal matrix elements $\langle He\rangle_{sG}$. The terms dropped in obtaining Eqs. (68) are of order $(mva_0/\hbar)^2$ or smaller.

Eqs. (68) are readily solved if the diabatic terms (if any) are neglected; γ_{Gm} and u_{Gm} are then given by ratios of sums involving standard matrix elements. In the coefficients of γ_{Gm} and u_{Gm} the well-known oscillator strength sums can be recognized. The solutions for state G interpolate smoothly between the united-atom and separated-atom limits.

The diversity of level schemes for diatomic molecules makes it hard to guarantee that Eqs. (66) or (68) will always possess satisfactory solutions. The following strategy should usually be effective however. One first introduces diabatic states to treat all narrow avoided crossings. By narrow we mean widths less than about one-half an atomic unit. The goal is to have slowly varying translational factors and not have them switch suddenly to follow a rapidly changing adiabatic state.

The purpose is to minimize the size of the derivatives of γ_G and u_G in Eq. (67) and Eq. (40). Having obtained a suitable mixed basis of adiabatic and diabatic states, one solves Eqs. (66) for low velocities. The narrow avoided crossings tend to have small off-diagonal diabatic coupling matrix elements $(\bar{H}_e)_{rs}$. Those of order .01 a.u. or less can probably be omitted from Eqs. (66). With luck all the diabatic terms can be neglected and the γ_G and u_G are readily determined. Otherwise, new matrix elements such as $(x_m x_m)_{GS}$ and $(z_m H_e)_{rG}$ are required in order to include large diabatic terms. At higher velocities satisfying $mva_o/\hbar \geq 1$, the power series approach gets increasingly bad. However, in the separated-atom limit the one-state solution is valid at all velocities. Thus the velocity dependence of γ_{Gm} and u_{Gm} will show up in the transition region.

Since the low-velocity solution should be good up to $mva_o/\hbar \sim 0.3$ it is reasonable to try to solve Eqs. (66) by iteration, using the low-velocity values of γ_{Gm} and u_{Gm} to compute the first estimate of the $\bar{\gamma}_{GG}$ for the matrix elements in Eqs. (66) and (67). With fixed matrix elements, these equations become linear equations and thus more amenable to numerical treatment. Other schemes are conceivable. The derivative terms in Eq. (67) are small except as $mva_o/\hbar$ approaches unity, and even then will not be of major importance if $d\gamma_{Gm}/dR$ and du_{Gm}/dR are kept small. For this reason it is probably best to evaluate these terms using the previous γ_{Gm} and u_{Gm} in the iterations and find the new values by solving linear algebraic equations. Finally, it may be possible to omit the diabatic coupling. The crucial question concerns the convergence of any proposed scheme to solve Eqs. (66). This remains to be tested when computer programs for the required matrix elements are available.

IV. A LOW-VELOCITY QUANTAL APPROXIMATION TO THE LAGRANGIAN OF PAPER I[2]

In this section the Lagrangian of Ref. 2 (Eq. 69) is reconsidered in the limit of very low velocities. We have in mind the region of impact energies of a few atomic units or less, i.e., the region in which the semiclassical treatment cannot be used with confidence. In this velocity region, terms of order $(m/M)(Mv/\hbar)^2$ in Eq. (71)[2] may not be large compared to the small terms of order a_0^{-2}, some of which were omitted from Eq. (71).[2] The omitted terms come from the potential energy via Eq. (51)[2] and from Eq. (45).[2] Let the addition to C_{GO}^K of Eq. (71)[2] be called ΔC_{GO}^K. Then

$$\frac{-2M\xi_G}{\hbar^2}\,\Delta C_{GO}^K = \left\{\frac{2M}{\hbar^2}\,\Delta V + \left(\frac{M}{M_A+M_B}+\gamma_G^2\right)\left(\Delta\xi_G - \frac{\dot{\xi}^2}{\alpha_G^2}\right)\right.$$

$$+\left(4\frac{d\gamma_G}{dR}+R\frac{d^2\gamma_G}{dR^2}\right)\frac{\partial}{\partial\xi_G}$$

$$\left.+\left(2\gamma_G R\frac{d\gamma_G}{dR}+\left(R\frac{d\gamma_G}{dR}\right)^2\right)\frac{\partial^2}{\partial\xi_G^2}\right\} A_G R_{GG'}(\xi_G)\,. \qquad (69)$$

The $-\dot{\xi}^2$ term in Eq. (69) allows for the fact that the azimuthal dependence of $\chi_G=(2\pi)^{-\frac{1}{2}}A_G e^{i\Lambda\xi_G}$ has been already integrated out in Eq. (I-69). The potential difference ΔV is defined in Eq. (I-51). With the addition of ΔC_{GO}^K to C_{GO}^K in Eq. (I-71) the terms neglected in Eqs. (I-69) are at most of order $(m/M)^2\partial^2 R_{GG'}/\partial\xi_G^2$, $(m/M)a_o^{-1}\partial R_{GG'}/\partial\xi_G$, and $(m/M)a_o^{-2}R_{GG'}$. The first is of the order of an $(m/M)^2$ correction to the heavy particle reduced mass. The

second is an m/M correction to the radial coupling, and the third is of the order of an m/M' correction to the electron reduced mass terms. The above terms should be negligible for practical purposes.

To get the equations to decouple in the separated-atom limit we include the electron-reduced mass terms from Eq. (69) in the definition of the electronic basis functions according to

$$\left(-\frac{\hbar^2}{2}\left(\frac{1}{m} + \frac{1}{M_A + M_B} + \frac{\mu_G(R)}{M}\right)\nabla_r^2 + V - \epsilon_G \right)\chi_G' = 0 \ . \qquad (70)$$

This can be done by applying perturbation theory to the usual fixed-nucleus eigenfunctions χ_G. However, it turns out that the final equations can be expressed in terms of matrix elements containing only the fixed-nucleus functions. The χ_G' need not be calculated explicitly.

The first approximation used to simplify Eq. (69)[2] is a series expansion for $d^J_{\Omega,\Omega'}(\theta)$ in Eq. (69).[2] We use

$$d^J_{\Omega,\Omega'}(\theta) = \delta_{\Omega,\Omega'}\left\{1 - \tfrac{1}{2}(j(j+1) - \Omega^2)\beta^2\right\} - \tfrac{1}{8}\beta\left\{\delta_{\Omega,\Omega'+1}\sqrt{(j+\Omega)(j-\Omega')}\right.$$

$$\left. - \delta_{\Omega,\Omega'-1}\sqrt{(j-\Omega)(j+\Omega')}\right\} + \frac{\beta^2}{8}\left\{\delta_{\Omega,\Omega'+2}\sqrt{(j+\Omega)(j+\Omega-1)(j-\Omega')(j-\Omega'-1)}\right.$$

$$\left. + \delta_{\Omega,\Omega'-2}\sqrt{(j+\Omega')(j+\Omega'-1)(j-\Omega)(j-\Omega-1)}\right\} + O(\beta^3 j^3) \ , \qquad (71)$$

where $\vec{r} = \vec{r}_{1G} - \vec{r}_{2G} = (m/M)(\vec{r}_G/r_G)(r_G - r'_G)$. We will evaluate $\vec{r}$ to first order in (m/M) which for small j is not consistent with keeping the second-order terms in Eq. (71). However we are primarily interested in relatively large j and the error is very small in any event. Equation (71) is an expansion in $(m/M)j \sim mbv/\hbar$, where b is the collision impact parameter and v the impact velocity. We are interested in impact energies for which $Mv^2/2 \lesssim mv_0^2/2$. Thus $v \lesssim (m/M)^{\frac{1}{2}}v_0$ and $(m/M)j \lesssim (m/M)^{\frac{1}{2}}$. Here v_0 stands for the atomic unit of velocity. The use of Eq. (71) reduces the effective extent of the allowed angular coupling in Eq. $(69)^2$ considerably.

The second approximation is to apply Taylor's expansion to express all functions of $\vec{r}_G, \vec{r}'_G$ in terms of functions of $\vec{r}_G, \vec{r}'_G$. The object is to remove the radial scattering functions from the electronic coordinate integration over $d\vec{r}_G d\vec{r}'_G$ in Eq. $(69)^2$ and to make the variables in both electronic functions the same. Sometimes the new term from Taylor's expansion is of the same order as terms already neglected. If not, the new term is retained.

Let us express the final approximate Lagrangian to be derived from Eq. $(69)^2$ in the form

$$\dot{R}_{G'} = -\tfrac{1}{4}(2K+1)(-1)^M \delta_{K'-K} A_K A_{K'} \left(\frac{\pi}{2M}\right) \sum_G \sum_{\bar{G}} (-1)^{\frac{1}{2}(\bar{G}+G)} \int_0^\infty dR\, R^{\bar{G}}_{\bar{G}G'}(R)$$

$$\cdot \left\{ S_{\bar{G}G} \frac{d}{dR} + 2V_{\bar{G}G} \frac{d}{dR} + M_{\bar{G}G} \right\} R_{GG'}(R) \qquad (72)$$

Here $R_{G'}$ stands for the right-hand set of functions $R_{GG'}$ and $R_{\bar{G}'}$ stands for the left hand set $R_{\bar{G}\bar{G}'}$. As in the previous sections $G=n$, $\bar{G}=\bar{n}^-$, $\bar{G}=\bar{n}-^-$. In Eq. (72) the integration variable ξ_G has been renamed R and S, V, and M are real matrix functions of R yet to be identified. Note that the approximation contemplated here does not envisage coupled equations of higher order than second, whereas a direct application of Taylor's expansion to the second derivative terms in Eqs. $(69)^2$ and $(71)^2$ leads to third derivative terms. These third-derivative terms will be dropped because as the function $R_{GG'}(\xi_G)$ varies less and less rapidly its second derivative can be treated with less accuracy than the lower derivatives. We shall return to this point later, when the consequences of the assumption have been worked out. In Eq. $(71)^2$ consider all the terms which are proportional to $R_{GG'}(\xi_G)$ after $\partial/\partial\xi_G$ and $\partial/\partial\xi_{\bar{G}}$ have been applied to $A_G R_{GG'}$. All the terms with a factor m/M are to be dropped because they are of the same order as terms omitted from Eqs. $(71)^2$ and (69). In the remaining terms of Eq. $(71)^2$ introduce

$$R_{GG'}(r_G) = R_{GG'}(r_{\bar{G}}) + \frac{dR_{GG'}}{dr_{\bar{G}}}(r_{\bar{G}})\,(r_G - r_{\bar{G}}) + \frac{1}{2}\frac{d^2R_{GG'}}{dr_{\bar{G}}^2}(r_{\bar{G}})\,(r_G - r_{\bar{G}})^2 \qquad (73)$$

where $r_G - r_{\bar{G}}$ is given by Eq. (10) and is of order $(m/M)a_0$. With the use of Eq. (73) the radial scattering functions can be removed from the electron integrals in Eq. (I-69). Only the terms in $dR_{GG'}/dr_{\bar{G}}$ from r_G in C^k_{GO} and from the first term of $C^k_{G\pm1}$ need be retained. Their contribution to $2V_{GG}$ of Eq. (72) is

$$2V^{(1)}_{GG} = \frac{m}{M}\,r_{\bar{G}}\left\{(\gamma_G - \gamma_{\bar{G}})\,R^k_{GG} + (u_G - u_{\bar{G}})\,\langle z\rangle_{GG}\right\}$$

$$+ \frac{m}{M}\,r_{\bar{G}}^2\left(\frac{m}{2M}\right)\left\langle\frac{\gamma_G - \gamma_{\bar{G}}}{R}\right\rangle\left\{\sqrt{(K+\bar{K})(K-\bar{K})}\left[(\gamma_G^2 - \gamma_{\bar{G}}^2)\langle x^+\rangle_{GG}\right.\right.$$

$$\left. + (u_G - u_{\bar{G}})\,\langle x^+ z\rangle_{GG}\right] - \sqrt{(K-\bar{K})(K+\bar{K})}\left[(\gamma_G^2 - \gamma_{\bar{G}}^2)\langle x^-\rangle_{GG}\right.$$

$$\left.\left. + (u_G - u_{\bar{G}})\,\langle x^- z\rangle_{GG}\right]\right\}$$

$$+ \frac{m}{M}\,\frac{\sqrt{(K+\bar{K})(K-\bar{K})}}{R^2}\left\langle\left\langle R\,(\gamma_G^2 - \gamma_{\bar{G}}^2) + (u_G - u_{\bar{G}})\,z\right\rangle\left\langle\frac{L^+}{\hbar} + R\gamma_G v^+\right\rangle\right\rangle_{GG}$$

$$+ \frac{m}{M}\,\frac{\sqrt{(K-\bar{K})(K+\bar{K})}}{R^2}\left\langle\left\langle R\,(\gamma_G^2 - \gamma_{\bar{G}}^2) + (u_G - u_{\bar{G}})\,z\right\rangle\left\langle\frac{L^-}{\hbar} - R\gamma_G v^-\right\rangle\right\rangle_{GG} \qquad (74)$$

In Eq. (74) $u_G = \kappa_G - k_{ii}R$. Note that $\vec{r}$ locates the electron with respect to the center of mass of the nuclei; xyz are the body-fixed components of $\vec{r}$, $x^{\pm} = x \pm iy$, $L^{\pm} = L_x \pm iL_y$, etc. The orbital angular momentum operator $\vec{L}$ is computed with respect to the center of mass of the nuclei. Finally,

$$\langle O \rangle_{\bar{G}G} = \int d\vec{r}\, \chi^*_{\bar{G}}\, O \chi_G \quad , \tag{75}$$

where O is an operator and the χ_G are the usual fixed-nucleus eigenfunctions without electron reduced-mass effects. In obtaining Eq. (74) all order m/M coordinate differences other than that from Eq. (73) were dropped. The first term in Eq. (74) is the most important since by assumption $(m/M)\vec{r}_G$ is of order a_0. Indeed, from Eq. (8) it is seen that as E and K go to zero $(m/M)\vec{r}_G$ approaches $-(2m/\hbar^2)\vec{r}_G$. The remaining terms in Eq. (74) are of order $mva_0/\hbar$ smaller.

The last term in Eq. (73) contributes

$$S^{(0)}_{\bar{G}G} = \frac{1}{2}\left(\frac{m}{M}\right)^2 \vec{r}_G \left\langle \left[R(\vec{\kappa}_{\bar{G}} - \vec{\kappa}_G) + (u_{\bar{G}} - u_G)\, z \right] \right\rangle_{\bar{G}G} \tag{76}$$

to $S_{\bar{G}G}$. Finally the expression for $H_{\bar{G}G}$ is obtained by adding up all the terms in Eq. (71)[2] and (69) which come from $R_{GG'}(\xi_{\bar{G}})$ in Eq. (73). An expression for $H_{\bar{G}G}$ will be given later.

Consider next the terms from Eq. (71)^2 containing $dR_{GG'}/d\vec{r}_G$ after differentiation of $A_G R_{GG'}$ with respect to $\vec{r}_G$. In these terms we insert

$$\frac{dR_{GG'}}{d\vec{r}_G}\ (\vec{r}_G) = \frac{dR_{GG'}}{d\vec{r}_{\bar{G}}}\ (\vec{r}_{\bar{G}}) + \frac{d^2R_{GG'}}{dr_{\bar{G}}^2}\ (\vec{r}_{\bar{G}})\ (\vec{r}_G - \vec{r}_{\bar{G}})\ . \tag{77}$$

The first derivative terms from Eq. (77) contribute

$$\begin{aligned} 2V_{\bar{G}G}^{(2)} = {} & 2\left\langle \frac{\partial}{\partial R} \right\rangle_{\bar{G}G} - 2u_G \left\langle \frac{\partial}{\partial z} \right\rangle_{\bar{G}G} \\ & - \frac{m}{M} \frac{(\vec{r}_{\bar{G}} - \vec{r}_G)}{R} \sqrt{(K + \bar{z})(K - z)}\ \left\langle x^+ \left(\frac{\partial}{\partial R} - u_G \frac{\partial}{\partial z} \right) \right\rangle_{\bar{G}G} \\ & + \frac{m}{M} \frac{(\vec{r}_{\bar{G}} - \vec{r}_G)}{R} \sqrt{(K - \bar{z})(K + z)}\ \left\langle x^- \left(\frac{\partial}{\partial R} - u_G \frac{\partial}{\partial z} \right) \right\rangle_{\bar{G}G} \\ & + \frac{m}{M} \frac{\left(d_{\vec{r}_G} - k_G R \right)}{R} \left| \sqrt{(K + \bar{z})(K - z)}\ \langle x^+ \rangle_{\bar{G}G} - \sqrt{(K - \bar{z})(K + z)}\ \langle x^- \rangle_{\bar{G}G} \right| \end{aligned} \tag{78}$$

to $V_{\bar{G}G}$ in Eq. (72). In all,

$$V_{\bar{G}G} = V_{\bar{G}G}^{(1)} + V_{\bar{G}G}^{(2)}\ . \tag{79}$$

The first two terms in Eq. (78) are of order a_o^{-1}; the others are order $mva_o/\hbar$ smaller. The second-derivative terms from Eq. (77) contribute to $S_{\bar{G}G}$ in Eq. (72). Calling them $S^{(2)}_{\bar{G}G}$ we have

$$S^{(2)}_{\bar{G}G} = \frac{2m}{M}\left\langle\left[(\dot{r}_{\bar{G}} - \dot{r}_G)R + (u_{\bar{G}} - u_G)z\right]\left[\frac{\partial}{\partial R} - u_G\frac{\partial}{\partial z}\right]\right\rangle_{\bar{G}G} \quad . \tag{80}$$

In obtaining Eq. (80) a term of order $(m/M)(mva_o/\hbar)$ was dropped. The rest of the terms of $S_{\bar{G}G}$ come from those terms which contain $d^2R_{GG'}/dr_G^2$ after differentiation of $A_GR_{GG'}$ in Eq. (71).[2] We set

$$\frac{d^2R_{GG'}}{dr_G^2}(r_G) = \frac{d^2R_{GG'}}{dr_{\bar{G}}^2}(r_{\bar{G}}) \quad . \tag{81}$$

Then their contribution to $S_{\bar{G}G}$ is $S^{(1)}_{\bar{G}G} + S^{(3)}_{\bar{G}G}$ where

$$S^{(1)}_{\bar{G}G} = \delta_{\bar{G}G} - \frac{m}{2M}\frac{(\gamma_{\bar{G}} - \gamma_G)}{R}\left\{\sqrt{(K+\bar{\Lambda})(K-\Lambda)}\,\langle x^+\rangle_{\bar{G}G} - \sqrt{(K-\bar{\Lambda})(K+\Lambda)}\,\langle x^-\rangle_{\bar{G}G}\right\}$$

$$- \frac{1}{4}\frac{m^2}{M^2}\frac{(K(K+1)-\Lambda^2)}{R^2}\,(\gamma_{\bar{G}} - \gamma_G)^2\,\langle a^2\rangle_{\bar{G}G}$$

$$+ \frac{m^2}{8M^2}\frac{(\gamma_{\bar{G}} - \gamma_G)^2}{R^2}\left\{\sqrt{(K+\bar{\Lambda})(K+\bar{\Lambda}-1)(K-\Lambda)(k-\Lambda-1)}\,\langle(x^+)^2\rangle_{\bar{G}G}\right.$$

$$\left. + \sqrt{(K+\Lambda)(K+\Lambda-1)(K-\bar{\Lambda})(K-\bar{\Lambda}-1)}\,\langle(x^-)^2\rangle_{\bar{G}G}\right\}$$

$$+ \frac{m}{M}\left\{\left(R\gamma_{\bar{G}}\frac{d\gamma_{\bar{G}}}{dR} + \gamma_G k_{\bar{G}}R^2 + k_{\bar{G}}R^3\frac{d\gamma_{\bar{G}}}{dR}\right)\delta_{\bar{G}G} + \left(-4k_{\bar{G}}R - R^2\frac{dk_{\bar{G}}}{dR} + \frac{d\gamma_{\bar{G}}}{dR}\right)\langle z\rangle_{\bar{G}G}\right\}$$

$$- \frac{m}{M}\frac{u_{\bar{G}} - u_G}{R}\langle z\rangle_{\bar{G}G} + \frac{m}{M}\left\langle\left[\left(\gamma^2_{\bar{G}} - \gamma^2_G\right)R + (u_{\bar{G}} - u_G)z\right]\frac{\partial}{\partial R}\right\rangle_{\bar{G}G}$$

$$- \frac{m}{M}\left\langle\left[\left(\gamma^2_{\bar{G}} - \gamma^2_G\right)R + (\gamma_{\bar{G}} - \gamma_G)z\right]\left(\frac{\rho}{R}\right)\frac{\partial}{\partial\theta}\right\rangle_{\bar{G}G}$$

$$+ \frac{m}{M}\left\langle\left[R^2\frac{d\gamma_{\bar{G}}}{dR}\gamma^2_G + R\gamma^3_G - R^2\frac{d\gamma_{\bar{G}}}{dR}\gamma^2_{\bar{G}} - R\gamma^3_{\bar{G}} - (\gamma_G - \gamma_{\bar{G}})\frac{p^2}{R}\right.\right.$$

$$\left.\left. + \left(\gamma^2_G - \gamma^2_{\bar{G}} + R\gamma_G\frac{d\gamma_G}{dR} - R\gamma_{\bar{G}}\frac{d\gamma_{\bar{G}}}{dR} - \gamma_G k_G R^2 + \gamma_{\bar{G}}\,k_{\bar{G}}R^2 - R^3 k_G\frac{d\gamma_G}{dR}\right.\right.\right.$$

$$\left.\left.\left. + R^3 k_{\bar{G}}\frac{d\gamma_{\bar{G}}}{dR}\right)z\right]\frac{\partial}{\partial z}\right\rangle_{\bar{G}G} + \frac{m}{M}\,(1 - \delta_{\bar{G}G})(\gamma^2_{\bar{G}} - \gamma^2_G)\,(\epsilon_G - \epsilon_{\bar{G}})^{-1}(\hbar^2/2m)\,\langle\Delta_{\bar{F}}\rangle_{\bar{G}G} \quad , \quad (82)$$

and

$$S_{\bar{G}G}^{(2)} = \frac{m}{M}\left\langle -\gamma_G - 2R\gamma_G\frac{d\gamma_G}{dR} - 4R^2\gamma_G k_G + R^4 k_G^2 + 2\gamma_G R\left(k_G R - \frac{d\gamma_G}{dR}\right)\right.$$

$$\left. + \left(2k_G R + 2R^2\frac{dk_G}{dR} + 2\left(k_G R - \frac{d\gamma_G}{dR}\right)\right)z\right\rangle_{\bar{G}G} \quad . \tag{83}$$

In all,

$$S_{\bar{G}G} = S_{\bar{G}G}^{(0)} + S_{\bar{G}G}^{(1)} + S_{\bar{G}G}^{(2)} + S_{\bar{G}G}^{(3)} \quad . \tag{84}$$

The term $S_{\bar{G}G}^{(1)}$ comes entirely from the γ'/γ_G^2 term in Eq. (71).[2] The first four of its terms come from Eq. (71). The fifth term in Eq. (32) reflects the difference between $J_{\bar{G}}^{-1}$ and unity. The sixth term represents the difference between $\gamma_{\bar{G}}/\gamma_G$ and unity. The next three terms reflect the change of variables in A_G of Eq. (I-71) and the last term accounts for the electron reduced-mass effects in χ_G' of Eq. (70) assuming for simplicity that G and $\bar{G}$ are non-degenerate. The term $S_{\bar{G}G}^{(3)}$ comes entirely from the m/M terms in C_{GO} of Eq. (71).[2] All of the terms in $S_{\bar{G}G}$ except the first two terms of $S_{\bar{G}G}^{(1)}$ are of order m/M.

Let us return now to Eq. (72). It is not hard to show that the solutions of Eq. (72) will be compatible with unitarity provided

$$S^{*}_{\bar{G}\bar{\bar{G}}} = S_{\bar{\bar{G}}G} \ , \tag{85a}$$

$$\frac{dS_{\bar{G}\bar{\bar{G}}}}{dR} = V_{\bar{G}\bar{\bar{G}}} + V^{*}_{\bar{G}\bar{\bar{G}}} \ , \tag{85b}$$

$$\frac{d}{dR}\left(V_{\bar{G}\bar{\bar{G}}} - V^{*}_{\bar{G}\bar{\bar{G}}}\right) = M_{\bar{G}\bar{\bar{G}}} - M^{*}_{\bar{G}\bar{\bar{G}}} \tag{85c}$$

$$S_{\bar{n}-\bar{\Lambda},n-\Lambda} = S_{\bar{n}\bar{\Lambda},n\Lambda} \ ,$$

$$V_{\bar{n}-\bar{\Lambda},n-\Lambda} = V_{\bar{n}\bar{\Lambda},n\Lambda} \ ,$$

$$M_{\bar{n}-\bar{\Lambda},n-\Lambda} = M_{\bar{n}\bar{\Lambda},n\Lambda} \ . \tag{85d}$$

In the present case all the matrices are real, and, in addition, Eqs. (85d) are satisfied. If Eqs. (85) hold, a short calculation starting with Eq. (72) shows that

$$\mathcal{V}(R_{\bar{G}'},R_{G'}) - \mathcal{V}(R_{G'},R_{\bar{G}'}) = 4\pi\,(2K+1)(-1)^{M_K}\,\delta_{\bar{K}K'}\,\delta_{M_K\bar{M}_K}\left(\frac{\hbar}{2M}\right)$$

$$\times \sum_{\bar{G}}\sum_{G}(-1)^{\bar{\Lambda}+\Lambda}\int_{0}^{\infty} dR\ \frac{dF_{\bar{G}G}}{dR} \ , \tag{86}$$

with

$$F_{\bar{G}G}(R) = R_{\bar{G}\bar{G}'} S_{\bar{G}G} \frac{dR_{GG'}}{dR} - \frac{dR_{\bar{G}\bar{G}'}}{dR} S_{\bar{G}G} R_{GG'}$$

$$+ R_{\bar{G}\bar{G}'} \left[V_{\bar{G}G} - V^{*}_{G\bar{G}} \right] R_{GG'} \quad . \tag{87}$$

The work of Demkov[10,11] shows how detailed balancing and unitarity for the theory can be deduced from Eqs. (86) and (87).

How well are Eqs. (85a) and (85b) satisfied by $S_{\bar{G}G}$ and $V_{\bar{G}G}$? Calculations show that $V_{\bar{G}G}$ and just the first two terms of $S^{(1)}_{\bar{G}G}$ (i.e. the largest terms) satisfy equations (85a) and (85b). The m/M parts of $S_{\bar{G}G}$ (i.e. all the remaining terms) cannot play a role in Eq. (85b) since terms of this order have been dropped from $V_{\bar{G}G}$. Not all of the m/M contributions to $S_{\bar{G}G}$ are Hermitian symmetric either. Having omitted small terms from the exact Lagrangian in Ref. 2, we can only expect to satisfy the symmetry and unitarity conditions approximately. The approximation is a very good one as can be seen by noting for example the effect of an (m/M) error in $S_{\bar{G}G}$ on Eq. (87). It is smaller than the contribution of the $V_{\bar{G}G}$ terms which are frequently omitted.

We now give the expression for $M_{\bar{G}G}$. Its largest term comes from the ν^2_G group of terms in Eq. $(71)^2$, and so we put it first. In terms

of the matrix $S^{(1)}_{\bar{G}G}$ of Eq. (B2).

$$M_{\bar{G}G} = \gamma_G^2(R)\, S^{(1)}_{\bar{G}G} + \frac{m}{M}\frac{d}{dR}\left(\gamma_G^2\right)\left(u_{\bar{G}} - u_G\right)\langle z\rangle_{\bar{G}G}$$

$$+ \frac{m}{M}\left\langle \gamma_G^2 - 2k_G R z\right\rangle_{\bar{G}G}\frac{(K(K+1)-\Lambda^2)}{R^2} + \left\langle\frac{\partial^2}{\partial R^2}\right\rangle_{\bar{G}G} - \frac{1}{\hbar^2 R^2}\left\langle L_x^2 + L_y^2\right\rangle_{\bar{G}G}$$

$$-\left(\frac{d\gamma_G}{dR} + \frac{d}{dR}\left(R\frac{d\gamma_G}{dR}\right)\right)\left\langle\frac{\partial}{\partial z}\right\rangle_{\bar{G}G} - 2u_G\left\langle\frac{\partial}{\partial R}\frac{\partial}{\partial z}\right\rangle_{\bar{G}G} + \left(\gamma_G + R\frac{d\gamma_G}{dR}\right)^2\left\langle\frac{\partial^2}{\partial z^2}\right\rangle_{\bar{G}G}$$

$$+ 2\frac{\gamma_G}{R}\left(\left\langle z\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right)\right\rangle_{\bar{G}G} - \left\langle\rho\frac{\partial}{\partial\rho}\frac{\partial}{\partial z}\right\rangle_{\bar{G}G} - \left\langle\frac{\partial}{\partial z}\right\rangle_{\bar{G}G}\right) + \gamma_G^2\left\langle\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2}\right\rangle_{\bar{G}G}$$

$$- 2\left(\frac{d\gamma_G}{dR} + k_G R\right)\left\langle\frac{\partial}{\partial z}\right\rangle_{\bar{G}G} - 2\left(R\frac{d\gamma_G}{dR} + k_G R^2\right)\left(\gamma_G + R\frac{d\gamma_G}{dR}\right)\left\langle\frac{\partial^2}{\partial z^2}\right\rangle_{\bar{G}G}$$

$$+ \left(4\frac{d\gamma_G}{dR} + R\frac{d^2\gamma_G}{dR^2}\right)\left\langle\frac{\partial}{\partial z}\right\rangle_{\bar{G}G} + \left(2\gamma_G R\frac{d\gamma_G}{dR} + R^2\left(\frac{d\gamma_G}{dR}\right)^2\right)\left\langle\frac{\partial^2}{\partial z^2}\right\rangle_{\bar{G}G}$$

$$- \frac{2m}{\hbar^2}\left\langle\left(R\gamma_G^2 + u_G z\right)\frac{\partial V}{\partial R}\right\rangle_{\bar{G}G} + \frac{2m}{\hbar^2}\frac{\gamma_G}{R}\left\langle z\rho\frac{\partial V}{\partial z}\right\rangle_{\bar{G}G}$$

$$+ \frac{2m}{\hbar^2}\left(\gamma_G + R\frac{d\gamma_G}{dR}\right)\left\langle\left(R\gamma_G^2 + u_G z\right)\frac{\partial V}{\partial z}\right\rangle_{\bar{G}G} - \frac{2m}{\hbar^2}\frac{\gamma_G}{R}\left\langle\rho^2\frac{\partial V}{\partial z}\right\rangle_{\bar{G}G}$$

$$+\frac{2m}{\hbar^2}\,\gamma_G\left\langle\phi\,\frac{\Delta V}{\hbar^2}\right\rangle_{GG}+\frac{\sqrt{(K+\tilde{\imath})(K-\imath)}}{R^2}\left\langle\frac{L^+}{\hbar}+\gamma_G R^{y^+}\right\rangle_{GG}$$

$$+\frac{\sqrt{(K-\tilde{\imath})(K+\imath)}}{R^2}\left\langle\frac{L^-}{\hbar}-\gamma_G R^{y^-}\right\rangle_{GG}$$

$$+\frac{\sqrt{(K+\imath+1)(K-\imath)}}{R^2}\left(-\frac{m}{2M}\right)\frac{(\gamma_G-\gamma_G)}{R}\left\{\sqrt{(K+\tilde{\imath})(K-\imath-1)}\left\langle x^+\left(\frac{L^+}{\hbar}+\gamma_G R^{y^+}\right)\right\rangle_{GG}\right.$$

$$\left.-\sqrt{(K-\tilde{\imath})(K+\imath+1)}\left\langle x^-\left(\frac{L^+}{\hbar}+\gamma_G R^{y^+}\right)\right\rangle_{GG}\right\}$$

$$+\frac{\sqrt{(K-\imath+1)(K+\imath)}}{R^2}\left(-\frac{m}{2M}\right)\frac{(\gamma_G-\gamma_G)}{R}\left\{\sqrt{(K+\tilde{\imath})(K-\imath+1)}\left\langle x^+\left(\frac{L^-}{\hbar}-\gamma_G R^{y^-}\right)\right\rangle_{GG}\right.$$

$$\left.-\sqrt{(K-\tilde{\imath})(K+\imath-1)}\left\langle x^-\left(\frac{L^-}{\hbar}-\gamma_G R^{y^-}\right)\right\rangle_{GG}\right\}. \qquad (88)$$

In Eq. (88) the smallest terms retained are of order a_o^{-2}; we continue to assume that $(m/M)_C \sim a_o^{-2}$.

The last four terms in Eq. (88) come from $C^K_{G\pm1}$ in Eq. $(71)^2$, the terms with partial derivatives of V come from ΔV in Eq. (69), as do the preceding two terms. The rest of the terms come from C^K_{GO} in Eq. $(71)^2$. Eq. (88) can be simplified considerably. In particular, all of the terms with V cancel against terms in $\gamma_G S^{(1)}_{GG}$. Using Eq. (88) it is possible to verify the extent to which Eq. (85c) is satisfied.

Now in $V_{\bar{G}\bar{G}}$ the terms with selection rule $\Delta\ell=0$ are of order a_0^{-1} while the rest of the terms have selection rule $\Delta\ell=\pm1$ and are of order $(mva_0/\hbar)a_0^{-1}$. These latter terms cannot figure in Eq. (85) unless terms of order $(mva_0/\hbar)a_0^{-2}$ are retained in $M_{\bar{G}\bar{G}}$. However all such terms are omitted from Eq. (62), in which the smallest terms retained are of order a_0^{-2}. This simplifies the very long calculation considerably. The result is that Eq. (85c) is satisfied to within terms of order $(mva_0/\hbar)a_0^{-2}$ or $(m/M)a_0^{-2}$. The terms in $M_{\bar{G}\bar{G}}$ with selection rules $\Delta\ell=\pm1,\pm2$ are Hermitian symmetric; only terms with $\Delta\ell=0$ play a direct role in Eq. (85c).

Eqs. (72), (79), (84) and (86) specify a Lagrangian which is compatible with Eqs. (85)-(87) to a high degree of approximation for collisions in which $(m/M)k_G^2 \leq a_0^{-2}$ and $mva_0/\hbar \ll 1$. We take this to be a post-mortem justification for the use of Eq. (81) in off-diagonal terms.

The coupled equations are obtained by varying $\mathcal{Y}'$ of Eq. (72) with respect to $R^*_{\bar{G}\bar{G}'}$. For all $\bar{G}$

$$\sum_{\bar{G}} (-1)^{\bar{G}} \left\{ S_{\bar{G}\bar{G}} \frac{d^2}{dR^2} + 2V_{\bar{G}\bar{G}} \frac{d}{dR} + M_{\bar{G}\bar{G}} \right\} R_{\bar{G}\bar{G}'} = 0 \ . \tag{89}$$

As $R \to \infty$, $V_{\bar{G}\bar{G}}$ and $M_{\bar{G}\bar{G}}$ tend toward zero and $S_{\bar{G}\bar{G}}$ tends toward $\delta_{\bar{G}\bar{G}}$. Using an argument analogous to that which led to Eq. (46) from Eq. (42), equations for $u_H - \gamma_H - k_H R$ and γ_H are obtained by setting equal to zero the variation of $\mathcal{Y}'$ with respect to these parameters. Note

that $S_{\bar{G}G}$, $V_{\bar{G}G}$, and $M_{\bar{G}G}$ are functions of u_H, v_H and their first derivatives, so that the standard Euler-Lagrange equations can be used. In Section V the optimization will be carried out for the simplest case, that of a one-state expansion.

The above equations can be simplified considerably. However in simplifying the Lagrangian one has to be careful not to throw away so much that the optimization problem ceases to provide any information. Suppose that the parameters u_H and v_H are already determined, and consider Eq. (89). A substantial simplification is obtained by dropping all $\Delta\ell=\pm 2$ terms from $M_{\bar{G}G}$ and all $\Delta\ell=\pm 1$ terms from $V_{\bar{G}G}$. Then

$$V_{\bar{G}G} = \langle \frac{1}{R} \rangle_{\bar{G}G} - u_G \langle \frac{1}{z} \rangle_{\bar{G}G} + \frac{m}{2M} \kappa_G^2 (u_{\bar{G}} - u_G) \langle z \rangle_{\bar{G}G}$$

$$= \langle \frac{1}{R} \rangle_{\bar{G}G} + \frac{m}{2M} \langle z \rangle_{\bar{G}G} \left| \kappa_G^2 u_{\bar{G}} - \kappa_{\bar{G}}^2 u_G \right| . \qquad (90)$$

We now have $V^*_{\bar{G}G} + V_{\bar{G}G} = 0$. Thus to satisfy Eqs. (85) we use $S_{\bar{G}G} = \delta_{\bar{G}G}$. This approximation exhibits the usual selection rules for $V_{\bar{G}G}$ and $M_{\bar{G}G}$ while retaining the rest of the small a_o^{-2} terms in $M_{\bar{G}G}$. The next level of approximation is to drop the remaining a_o^{-2} terms in $M_{\bar{G}G}$ so that, with κ_G^2 from Eq. (8)

$$M_{\bar{G}G} = \gamma_{\bar{G}}^{\dagger}\gamma_G$$

$$+ \frac{\sqrt{(K+\bar{r})(K-r)}}{R^2}\left(\frac{L^+}{\hbar} + \gamma_G R\gamma^+ - \frac{m}{2M}\gamma_{\bar{G}}^{\dagger} R(\gamma_{\bar{G}} - \gamma_G)\, x^+\right) \bar{G}G$$

$$+ \frac{\sqrt{(K+\bar{r})(K-\bar{r})}}{R^2}\left(\frac{L^-}{\hbar} - \gamma_G R\gamma^- + \frac{m}{2M}\gamma_{\bar{G}}^{\dagger} R(\gamma_{\bar{G}} - \gamma_G)\, x^-\right) \bar{G}G \quad . \qquad (91)$$

In this approximation $M_{\bar{G}\bar{G}}^{*} = M_{\bar{G}G}$ and Eq. (85c) is violated to order a_0^{-2}. Eqs. (89)-(91) represent a simple but potentially useful approximate form of the theory. A similar equation has been derived by Albat and Gruen.[13] In this extreme simplification there is not enough information in $S_{\bar{G}G}$, $V_{\bar{G}G}$, and $M_{\bar{G}G}$ to determine γ_G and u_G from the Lagrangian. Thus their values must be found from a higher-level approximation.

V. ONE-STATE WAVE-THEORETIC OPTIMIZATION OF δ_G AND η_G

We return to Eq. $(69)^2$ for the special case in which there is but one term in the expansion (54).[2] This case is not an unreasonable one to consider in connection with low-velocity collisions. In Eq. $(69)^2$ we have $\bar{G}=G$ and hence we have $d^K_{\ldots}(\ldots-\ldots) = \ldots$. Since $\ldots$, the contributions from $C^K_{G\pm1}$ are automatically excluded. Moreover, there is no need to distinguish $\ldots_G$ from $\ldots_{\bar{G}}$ etc. and the radial scattering functions can be removed from the electron coordinate integrals. The Lagrangian $(69)^2$ therefore assumes without approximation the form (72),

$$\ldots = 4\pi(2K+1)\ldots_{RK}(-1)^{M_K}\ldots_{M_K M_K}\left(-\frac{\hbar^2}{2M}\right)\int_0^\infty dR\, R_{GG'}(R)$$

$$\times\left\{S_{GG}\frac{d^2}{dR^2}+M_{GG}\right\}R_{GG'} \quad , \qquad (92)$$

with $V_{GG}=0$. This time $\bar{G}=n-\ldots$. Although we are analyzing Eq. $(69)^2$ directly, the expressions for S_{GG} and M_{GG} can be taken from Section IV, since no approximations were involved in the treatment of the diagonal terms in Section IV. Thus, using the formulae of Section IV,

$$\omega_{GG} = \omega_{GG}^{(1)} + \omega_{GG}^{(-)}$$

$$\omega_{GG}^{(1)} = 1 + \frac{m}{M}\left[\omega_G + 2R\omega_G\frac{d\omega_G}{dR} - u_G\left(\omega_G + P\frac{d\omega_G}{dP}\right) + \left(\frac{du_G}{dP} - 2\frac{\omega_G - u_G}{P}\right)\langle z\rangle_{GG}\right],$$

$$\omega_{GG}^{(-)} = \frac{m}{M}\left[u_G - 2\omega_G - 4R\omega_G\frac{d\omega_G}{dR} - 2\frac{du_G}{dP}\langle z\rangle_{GG}\right],$$

$$M_{GG} = \omega_G S_{GG} + M_{GG}^{(1)}$$

$$M_{GG}^{(1)} = -\omega_G S_{GG}^{(-)} + \frac{m}{M}\left[\omega_G - 2\frac{(\omega_G - u_G)}{R}\langle z\rangle_{GG}\right]\left[\frac{\nu(\nu+1)}{R^2}\right]$$

$$+ \left(\frac{\dot{\rho}}{\rho R^2}\right)_{GG} - \frac{1}{\hbar^2 R^2}\left(L_x^2 + L_y^2\right)_{GG} - \omega_G\langle\rangle_{GG}$$

$$- \frac{2m}{\hbar^2}\frac{d\omega_G}{dR}\left(R\omega_G^2 + u_G\langle z\rangle_{GG}\right) . \qquad (93)$$

The decomposition of M_{GG} into $\omega_G S_{GG} + M_{GG}^{(1)}$ is for future convenience. The term $M_{GG}^{(1)}$ is of order a_0^{-2}. Actually ω_G enters into M_{GG} only as the coefficient of $S_{GG}^{(1)}$ as can be seen from Eq. (88).

The application of the variational principle to ψ of Eq. (92) is straightforward and is analogous to the calculation in Paragraph 4 of Ref. 10. However, one must ignore the negligible terms arising from the R-dependence of S_{GG}. The equation for $R_{GG'}$ is

$$\left\{ S_{GG} \left(\frac{d}{dR} + \cdots_G \right) + M^{(\cdot)}_{GG} \right\} R_{GG} = 0 \quad . \tag{94}$$

The same equation is satisfied by R_{GG}, and because of the boundary conditions at the origin we must have $R_{GG'} = e^{i} R_{GG}$, where $\cdot$ is a phase factor. In practice, at this point one can divide Eq. (94) by S_{GG} and note that it may be set equal to unity in the expression $M^{(1)}_{GG}/S_{GG}$. Let the integrand in Eq. (92) be called I. The Euler-Lagrange Equation for $\cdot_G$ arising from the variation with respect to $\cdot_G$ is

$$\frac{\partial I}{\partial \cdot_G} - \frac{d}{dR} \left(\frac{\partial I}{\partial \frac{d \cdot_G}{dR}} \right) = 0 \quad . \tag{95}$$

An analogous equation holds for u_G. From Eq. (93), taking into account $\cdot_G / \cdot_G$, we find

$$\frac{\partial I}{\partial \nu'_G} = P_{GG'}\left(\frac{d'}{dP} + \nu'_G\right) P_{GG'}\left\{-2\nu'_G - P u_G\left(\frac{m}{M}\right) + P_{GG'}P_{GG'}\nu'_G \frac{m}{M} 4P\nu'_G\right.$$

$$\frac{\partial I}{\partial \nu'_G} = R_{GG'}\left(\frac{d'}{dR} + \nu'_G\right) P_{GG'}\left(\frac{m}{M}\right)\left\{-2\nu'_G - 2P\frac{d\nu'_G}{dR} - u_G - \frac{2}{R}\langle z\rangle_{GG}\right\}$$

$$+ R_{GG'}R_{GG'}\left\{\nu'_G \frac{m}{M}\left(4\nu'_G + 4R\frac{d\nu'_G}{dR}\right) + \frac{m}{M}\left(2\nu'_G - 2\frac{\langle z\rangle_{GG}}{h}\right)\left(\frac{K(K+1)-\cdots}{P}\right)\right.$$

$$\left. - \frac{2m}{h}\frac{d\nu'_G}{dR} 2P\nu'_G\right\}$$

$$\frac{\partial I}{\partial \frac{du_G}{dR}} = R_{GG'}\left(\frac{d'}{dR} + \nu'_G\right) R_{GG'}\left(-\frac{m}{M}\right)\langle z\rangle_{GG} + R_{GG'}R_{GG'}\,2\nu'_G\frac{m}{M}\langle z\rangle_{GG}$$

$$\frac{\partial I}{\partial u_G} = R_{GG'}\left(\frac{d'}{dR} + \nu'_G\right) R_{GG'}\frac{m}{M}\left\{2u_G - \nu_G - R\frac{d\nu'_G}{dR} + \frac{2}{R}\langle z\rangle_{GG}\right.$$

$$+ R_{GG'}R_{GG'}\left\{\nu'_G\frac{m}{M}(-2u_G) + \frac{2m}{M}\frac{\langle z\rangle_{GG}}{R}\left(\frac{K(K+1)-\lambda^2}{R}\right)\right.$$

$$\left. - \frac{2m}{h^2}\frac{d\nu'_G}{dR}\langle z\rangle_{GG}\right\} \qquad (96)$$

From Eqs. (94) and (95) it can be seen that each term in Eq. (96) containing $\left(\frac{d}{dR} + \gamma_G\right)$ is of order r/M times the other term. Thus these terms can all be dropped. The Euler-Lagrange equation for u_G is

$$\gamma_{GG}\left\{P_{GG}\left[\frac{m}{M}\gamma_G(-2u_G) + \frac{m}{M}\langle z\rangle_{GG}\frac{d}{dR}\gamma_G\right]\right\}$$

$$= \frac{d}{dR}\left(R_{GG}P_{GG}\,2\gamma_G\frac{m}{M}\gamma_{GG}\right) . \qquad (97)$$

The equation for γ_G is

$$R_{GG}\left\{P_{GG}\left[\gamma_G\frac{m}{M}\left(4\gamma_G + 4R\frac{d\gamma_G}{dR}\right) + \frac{m}{M}\left(2\gamma_G - 2\frac{\langle z\rangle_{GG}}{R}\right)\left(\frac{K(K+1)-\lambda^2}{R^2}\right)\right.\right.$$

$$\left.\left. - \frac{2m}{M}\frac{d\gamma_G}{dR}2R\gamma_G\right]\right\}$$

$$= \frac{d}{dR}\left(R_{GG}P_{GG}\gamma_G\frac{m}{M}4R\gamma_G\right) . \qquad (98)$$

Note that the derivative of γ_G cancels out of Eq. (98). In Eq. (94) $\gamma_G = \gamma_{GG}(\ell)$. Therefore the parameters γ_G and u_G influence R_{GG} only weakly. In a first approximation the solutions of $(\frac{d^2}{dR^2} + \gamma_G^2)R_{GG}=0$ can be used in Eqs. (97) and (98) with the γ_G dependence of γ_G omitted. This provides formulae for u_G and γ_G.

A little study shows that the formulae are not useful very far into forbidden regions, where the wave functions are very small. For example using the JWKB approximation for a forbidden region with $k_G = (-\epsilon_G)^{1/2}$ we find

$$u_G = -\frac{d\langle z\rangle_{GG}}{dR} - 2k_G \langle z\rangle_{GG} \quad . \tag{99}$$

Near the turning point k_G is of order unity. Here the size of u_G is consistent with the basic assumption of Paper I that the z coordinate changes do not exceed order m/μ. However, far enough inside a forbidden region, k_G can become a_0^{-1} and the resulting value for u_G given by Eq. (99) is not acceptable. In such regions, because $R_{GG'} \to 0$, Eqs. (97) and (98) have nearly the form zero equals zero for all values of u_G and γ_G. The conclusion is that optimization to find u_G and γ_G fails in the forbidden regions, but that the use of any reasonable values should be all right.

Equations (97) and (98) exhibit problems in the allowed regions too. Each time $R_{GG'}$, R_{GG}, vanishes, u_G and γ_G have a singularity according to Eq. (97) or (98). This is undesirable from the conceptual point of view in which γ_G and u_G are thought to reflect the smooth transition from united-atom to separated-atom properties. It is also very impractical from a computational point of view. We assume that Eqs. (97) and (98) are to be solved after the high frequencies have been averaged out in the JWKB approximation. Then $R_{GG'}$, $R_{GG'}\gamma_G$ is nearly constant and can be factored out of Eqs. (97) and (98). The solutions are then

$$u_G = -\frac{d\langle z\rangle_{GG}}{dR}$$

$$\gamma_G = -\frac{\langle z\rangle_{GG}}{R} \tag{100}$$

These agree with the results obtained in Eq. (56) from the semi-classical version of the Lagrangian.

The passage from Eqs. (97) and (98) to Eq. (100) by averaging out the oscillations in $R_{GG'}$ $R_{GG'}$ is the method adopted here for seeking parameters u_G and λ_G which are slowly varying functions. Other ways to impose this restriction can be envisaged, as was mentioned in the Introduction to Reference 2.

Having obtained the "optimized" values (100), one wonders just how good the foregoing description of low-energy elastic scattering will turn out to be. Equations (100) do not satisfy the Euler-Lagrange equations exactly; however, they certainly make the variation of the Lagrangian functional small for slowly changing variations in λ_G and u_G when the JWKB approximation is valid for the radial function. Consider then the solving of Eq. (94) with λ_G and u_G from Eq. (100). From Eqs. (93) it is not hard to see that all dependence on λ_G and u_G occurs in terms of size a_o^{-2} compared to κ_G^2. No matter what λ_G and u_G of order unity are used, the effect on the phase shift is of the order of the effects adiabatic correction terms and mass polarization terms. These small corrections are probably hard to observe.[14] In the asymptotic region, Eqs. (100) and (94) provide a description of the scattering in which the atoms have their correct electron-reduced masses and the system reduced mass is correct to first order in m/M. This is conceptually desirable. However, it seems to the author that the domain of inelastic scattering at moderate velocities is the one most likely to provide examples where the ideas discussed in this paper and in Reference 2 have the most practical significance. One interesting case where the dynamics depends on the small a_o^{-2} terms directly is provided by homopolar-heteronuclear systems. Such a system has been recently discussed by Thorson and Delos.[6]

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