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Low-Energy Atom-Atom Scattering: Corrections to the He-He Interaction*

Marvin H. Mittleman and Hsiang Tai
Physics Department, The City College of the City University of New York, New York, New York 10031

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A formalism, previously presented, for describing atom-atom scattering in the adiabatic representation to higher orders in m/M is generalized to describe the problem of different isotopes and different atoms. This is accomplished by a sequence of nonlinear coordinate transformations which introduce a "switching function" which is defined only in the asymptotic limit of separated atoms. It is found that the effective potential for elastic scattering contains energy-dependent terms in order m/M and that it also depends upon the switching function in this order so that the potential is not unique. It is also found that in this order the definition of adiabatic states is not a trivial problem. A variational choice is made for the switching function and explicit calculations are presented for the He-He interaction. The coupled equations describing transitions are then derived and it is shown that terms are omitted from the usual coupling operator which are of the same order of magnitude as the one usually kept. This leads to a modification of the usual Landau-Zener transition formula.

I. INTRODUCTION

In a previous paper,[1] the low-energy scattering of two identical helium atoms was treated to higher orders in the parameter m/M. This was done because the interaction potential between He atoms is so small that small corrections may be appreciable. The question of whether a higher-order potential could be treated as local and energy independent was investigated. It was found that the nonlocality, entering from the dispersive part of the potential, was negligible, and that the energy dependence from the same source was also negligible.

In this paper we allow the two He atoms to have different masses and obtain the nuclear mass-dependent terms in the potential.[2] We also find energy dependence which is not negligible from a source which was omitted in I. We thereby have terms of relative order m/M in the potential which are both mass and energy dependent, but that are local.

The procedure used here is similar to that used in I for the equal-mass case: We define a scattering coordinate and an adiabatic Hamiltonian. As in the usual case we find that it is impossible to define a true adiabatic Hamiltonian. That is, if we require that (i) H_{ad} is symmetric in all electrons and has eigenfunctions which dissociate into antisymmetric products of atomic wave functions and (ii) that ξ enter only as a parameter so that $\vec{\nabla}_\xi$ does not enter into H_{ad}, then we find that there are still transitions between "adiabatic" states even when the local momentum of the atoms vanishes. However, we find here that the operator causing these transitions vanishes for separated atoms so that it may be diagonalized away in a limited basis set. This is discussed in Sec. II.

We are forced to introduce a "switching function"[3] $f(\vec{x},\vec{\xi})$(here $\vec{x}$ is an electron coordinate in order to define both $\vec{\xi}$ and H_{ad}). The function has the property that the factors $\frac{1}{2}(1\pm f)$ are, in the limit of separated atoms, projection operators for the electron into one or the other atom. The corrections to the interatomic potential depend upon this function which is arbitrary except for its boundary conditions. We are therefore led to the conclusion that the interatomic potential is not uniquely defined in the m/M terms. Nevertheless, we use a scattering variational criterion to define the switching function which, at most energies, turns out to depend only on the bound-state functions. The resulting equation is then crudely solved for the switching function which is then substituted back to obtain the mass- and energy-dependent terms in the potential.

In Sec. IV we turn to the coupled-channel problem in this formalism. We find that the coupling operator between two states is not $\sim\langle n|\vec{\nabla}_R|m\rangle\cdot\vec{\nabla}_R$ as in the usual theories but has additional terms which depend upon the switching function. It is pointed out that these additional terms make the coupling operator vanish at $R\to\infty$ where the above form does not. The additional terms also have the effect of coupling states of opposite parity, whereas the usual theory leaves them uncoupled.

In Sec. V we turn to the problem of dissimilar atoms and the problem of rearrangement collisions. The method used is a slight generalization of that in I. This is necessary in order to allow for the dissociation into different configurations of electrons. The example used is He + H where we allow for neutral final states or ions $He^+ + H^-$. We find similar results and that the transition operator is not the expectation of $\vec{\nabla}_\xi$ but something that involves the switching function also. This will have great importance when *a priori* calculations of Landau-Zener transition rates are attempted.

We turn here to the problem of the low-energy scattering of two helium atoms of different masses using the method of I.[4]

II. FORMULATION OF PROBLEM

We seek an expansion of the total wave function of the form

$$\Psi^{(\pm)}=\Sigma_n U_n(X,\vec{\xi})F_n^{(\pm)}(\vec{\xi}), \tag{2.1}$$

where X is the collection of all electron coordinates and where the U_n are adiabatic wave functions which, in the $\xi\rightarrow\infty$ limit, become products of atomic wave functions. The boundary conditions on the scattering functions are

$$F_n^{(\pm)}\rightarrow \delta_{no}e^{i\vec{p}\cdot\vec{\xi}}+(1/\xi)e^{ip_n\xi}f_n^{(\pm)}(\vec{\xi}), \tag{2.2}$$

where p is the incident momentum. The scattering coordinate must take the appropriate form in all portions of configuration space into which the atoms can dissociate. For example, the ground state can break up into the configuration

$$(\vec{R}_1\vec{r}_1\vec{r}_2),\quad(\vec{R}_2\vec{r}_3\vec{r}_4).$$

Here $\vec{R}_1,\vec{R}_2$ are the coordinates of the nuclei with masses M_1 and M_2, respectively, and $\vec{r}_i$ are electron coordinates. We call this the reference configuration. The scattering coordinate must also describe the asymptotic situation in which for example, electrons 1 and 3 are exchanged. Toward that end a new set of coordinates is introduced through the nonlinear transformation

$$\begin{aligned}\vec{R}_1&=\vec{\rho}+\frac{\mu}{M_1}\left[\vec{\xi}-\frac{m}{\mu}\Sigma_i\vec{x}_i\left(\frac{1+f_i}{2}\right)\right],\\ \vec{R}_2&=\vec{\rho}-\frac{\mu}{M_2}\left[\vec{\xi}+\frac{m}{\mu}\Sigma_i\vec{x}_i\left(\frac{1-f_i}{2}\right)\right],\\ \vec{r}_i&=\vec{\rho}+\vec{x}_i,\end{aligned} \tag{2.3}$$

where the switching functions f_i are restricted by

$$\begin{aligned}&f_i=f(\vec{x}_i,\vec{\xi}),\\ &\lim_{\xi\rightarrow\infty}f_i\rightarrow\begin{cases}+1 & \text{for } \vec{x}_i\rightarrow\dfrac{\mu}{M_1+2m}\vec{\xi}\\ -1 & \text{for } \vec{x}_i\rightarrow\dfrac{-\mu}{M_2+2m}\vec{\xi}.\end{cases}\end{aligned} \tag{2.4}$$

Here μ is the reduced mass of the atoms

$$\mu=\frac{(M_1+2m)(M_2+2m)}{M_1+M_2+4m} \tag{2.5}$$

and we introduce a mass-asymmetry parameter by

$$\lambda=\frac{M_1-M_2}{M_1+M_2+4m}. \tag{2.6}$$

The inverse of (2.3) is given by

$$\begin{aligned}\vec{\xi}&=\frac{M_1}{M_1+2m}\vec{R}_1-\frac{M_2}{M_2+2m}\vec{R}_2+\frac{m}{2\mu}\Sigma_i[\vec{r}_i(f_i-\lambda)-\vec{\rho}f_i],\\ \vec{\rho}&=\frac{M_1\vec{R}_1+M_2\vec{R}_2+m\Sigma_i\vec{r}_i}{M_1+M_2+4m},\quad \vec{x}_i=\vec{r}_i-\vec{\rho}.\end{aligned} \tag{2.7}$$

Hence $\vec{\rho}$ is the coordinate of the center of mass of the entire system and is ignorable. In the asymptotic limit in any particular configuration, $\vec{\xi}$ becomes the coordinate connecting the centers of mass of the two atoms. For example, in the reference configuration we get the limit

$$\vec{\xi}\rightarrow\frac{M_1\vec{R}_1+m(\vec{r}_1+\vec{r}_2)}{M_1+2m}-\frac{M_2\vec{R}_2+m(\vec{r}_3+\vec{r}_4)}{M_2+2m}.$$

We shall need the Jacobian of this transformation later. A straightforward but lengthy calculation results in

$$J\left(\frac{\vec{R}_1\vec{R}_2\vec{r}_i}{\vec{\rho}\vec{\xi}\vec{x}_i}\right)=\left(\frac{M_1+2m}{M_1}\right)^3\left(\frac{M_2+2m}{M_2}\right)^3\times\left[1-\frac{m}{2\mu}\Sigma_i\vec{x}_i\cdot\vec{\nabla}_\xi f_i+O\left(\frac{m}{\mu}\right)^2\right]. \tag{2.8}$$

It is now a simple task to rewrite the total kinetic energy in the new variables. The original form is, in units in which $\hbar=1$,

$$T=-\frac{1}{2M_1}\nabla_{R_1}{}^2-\frac{1}{2M_2}\nabla_{R_2}{}^2-\frac{1}{2m}\Sigma_i\nabla_{r_i}{}^2$$

and dropping all derivates $\vec{\nabla}_\rho$, the result is

$$T=a_{\mu\nu}\partial_{\xi_\mu}\partial_{\xi_\nu}+\beta_\mu\partial_{\xi_\mu}+\bar{\gamma}, \tag{2.9}$$

where

$$\begin{aligned}a_{\mu\nu}=&-\frac{1}{2\mu}\delta_{\mu\nu}-\frac{m}{2\mu^2}\Sigma_i(\partial_{\xi_\nu}x_{i\mu}f_i)\\ &+\frac{m\lambda}{8\mu^2}\Sigma_i[(\nabla_{i_\mu}x_{i\nu}f_i)+(\nabla_{i_\nu}x_{i\mu}f_i)]\\ &-\frac{m}{8\mu^2}\Sigma_i[(\nabla_{i_\sigma}x_{i\mu}f_i)(\nabla_{i_\sigma}x_{i_\nu}f_i)-\delta_{\mu\nu}]\\ &+O\left(\frac{m^2}{\mu^3}\right),\end{aligned} \tag{2.10a}$$

$$\beta_\mu=\frac{\lambda}{2\mu}\Sigma_i\nabla_{i_\mu}-\frac{1}{4\mu}\Sigma_i[\nabla_i{}^2,x_{i\mu}f_i]+O\left(\frac{m}{\mu^2}\right), \tag{2.10b}$$

$$\bar{\gamma}=-\frac{1}{2m}\Sigma_i\nabla_i{}^2+\frac{1}{2(M_1+M_2)}(\Sigma_i\vec{\nabla}_i)^2+O\left(\frac{m}{\mu^2}\right), \tag{2.10c}$$

where $\vec{\nabla}_i=\vec{\nabla}_{x_i}$.

We now turn to the problem of the construction of the adiabatic Hamiltonian H_{ad}. The problem is one of constructing a Hamiltonian which is symmetric in all electrons and which in the references configuration, with $\xi\rightarrow\infty$, is just the sum of two noninteracting atomic Hamiltonians. The method is again a simple generalization of the one used in I. A first try is

$$H_{\mathrm{ad}}'=-\frac{1}{2}\left(\frac{1}{m}-\frac{1}{2\mu}\right)\Sigma_i\nabla_i^2-\frac{\lambda}{8\mu}\Sigma_i(f_i\nabla_i^2+\nabla_i^2 f_i)$$
$$+\frac{1}{4\mu}\sum_{i>j}\left[\left(\frac{1+f_if_j}{2}\right)\vec{\nabla}_i\cdot\vec{\nabla}_j+\vec{\nabla}_i\cdot\vec{\nabla}_j\left(\frac{1+f_if_j}{2}\right)\right]$$
$$-\frac{\lambda}{4\mu}\sum_{i>j}\left[\left(\frac{f_i+f_j}{2}\right)\vec{\nabla}_i\cdot\vec{\nabla}_j+\vec{\nabla}_i\cdot\vec{\nabla}_j\left(\frac{f_i+f_j}{2}\right)\right]+V, \tag{2.11}$$

where V is just the usual potential energy rewritten in the new coordinates[5]:

$$V=\sum_{i>j}\frac{e^2}{x_{ij}}-2e^2\Sigma_i\left(\left|\vec{x}_i-\frac{\mu}{M_1}\vec{\xi}+\frac{m}{M_1}\vec{S}_+\right|^{-1}\right.$$
$$\left.+\left|\vec{x}_i+\frac{\mu}{M_2}\vec{\xi}+\frac{m}{M_2}\vec{S}_-\right|^{-1}\right)$$
$$+\frac{4e^2}{|(\mu/\mu_0)\vec{\xi}-(m/2\mu_0)\Sigma_i\vec{x}_i(f_i-\lambda_0)|}, \tag{2.12}$$

where

$$\vec{S}_\pm=\Sigma_i\vec{x}_i\left(\frac{1\pm f_i}{2}\right) \tag{2.13}$$

and the subscripts 0 on μ and λ indicate that we set $m=0$ in μ and λ to 2.5 and 2.6. H_{ad} is a perfectly adequate adiabatic Hamiltonian. It satisfies the two criteria laid down for H_{ad} in Sec. I. We shall, however, modify it so that it is Hermitian with respect to the weighting function J [Eq. (2.8)]. That is, we require

$$\int(dX)JuH_{\mathrm{ad}}v=\int(dX)JvH_{\mathrm{ad}}u \tag{2.14}$$

for arbitrary functions u and v. This can be accomplished by replacing the gradient operators $\vec{\nabla}_i$ by $\vec{\nabla}_i+(1/2J)\vec{\nabla}_iJ$, which we note from Eq. (2.8) is a correction of order m/μ. If we retain terms no smaller than $1/\mu$, then the adiabatic Hamiltonian

$$H_{\mathrm{ad}}=H'_{\mathrm{ad}}-(1/2m)\Sigma_i\frac{1}{J}\vec{\nabla}_iJ\cdot\vec{\nabla}_i$$
$$=H'_{\mathrm{ad}}+(1/2\mu)\Sigma_i\vec{\nabla}_i(\vec{x}_i\cdot\vec{\nabla}_\xi f_i)\cdot\vec{\nabla}_i=T_{\mathrm{ad}}+V. \tag{2.15}$$

We define a set of adiabatic wave functions from this by

$$[W_n(\xi)-H_{\mathrm{ad}}(X,\vec{\xi})]U_n(X,\vec{\xi})=0, \tag{2.16}$$

with the orthogonality property

$$\int dXJU_n^*U_{n'}=\delta_{nn'}. \tag{2.17}$$

If the operator H_{ad} is expanded in powers of m/μ then we also obtain W_n as a power series in this parameter. The zero-order result is identical with the usual molecular wave functions.

The exact elastic-scattering equation can be written[6]

$$\langle 0|E-H-H\frac{Q}{E^+-QHQ}H|0\rangle F_0^{(+)}(\vec{\xi})=0, \tag{2.18}$$

where $E=E_p+W_0(\infty)$ and where $\langle 0|\cdots|0\rangle$ indicates expectation with respect to U_0 (with J in the integral) for fixed $\vec{\xi}$ and where Q is a projection operator projecting onto the entire X space excluding only the state U_0. Neglecting the dispersive term for the moment the equation becomes

$$\langle 0|E-H|0\rangle F_0^{(+)}=\langle 0|E-W_0(\xi)-T_\xi|0\rangle F_0^{(+)}=0, \tag{2.19}$$

where

$$T_\xi=H-H_{\mathrm{ad}}=T-T_{\mathrm{ad}} \tag{2.20}$$

and T_{ad} can be gotten from (2.16). We write T_ξ in the form

$$T_\xi=a_{\mu\nu}\partial_{\xi_\mu}\partial_{\xi_\nu}+\beta_\mu\partial_{\xi_\mu}+\gamma, \tag{2.21}$$

where $a_{\mu\nu}$ and β_μ are given in (2.10) and

$$\gamma=\frac{1}{2}\left(\frac{1}{M_1+M_2}-\frac{1}{2\mu}\right)\Sigma_i\nabla_i^2+\frac{\lambda}{8\mu}\Sigma_i(f_i\nabla_i^2+\nabla_i^2f_i)+\frac{1}{M_1+M_2}\sum_{i>j}\vec{\nabla}_i\cdot\vec{\nabla}_j$$
$$-\frac{1}{2\mu}\sum_{i>j}\left[\left(\frac{1+f_if_j}{2}\right)\vec{\nabla}_i\cdot\vec{\nabla}_j+\vec{\nabla}_i\cdot\vec{\nabla}_j\left(\frac{1+f_if_j}{2}\right)\right]+\frac{\lambda}{2\mu}\sum_{i>j}\left[\left(\frac{f_i+f_j}{2}\right)\vec{\nabla}_i\cdot\vec{\nabla}_j+\vec{\nabla}_i\cdot\vec{\nabla}_j\left(\frac{f_i+f_j}{2}\right)\right]-\frac{1}{4\mu}\Sigma_i\vec{\nabla}_i(\vec{x}_i\cdot\vec{\nabla}_\xi f_i)\cdot\vec{\nabla}_i. \tag{2.22}$$

Then Eq. (2.19) can be rewritten

$$[E-W_0(\xi)-A_{00}^{\mu\nu}\partial_{\xi_\mu}\partial_{\xi_\nu}-B_{00}^{\mu}\partial_{\xi_\mu}-C_{00}]F_0^{(+)}(\vec{\xi})=0, \tag{2.23}$$

where

$$A_{nm}^{\mu\nu}(\xi)=\langle n|a_{\mu\nu}|m\rangle,$$
$$B_{nm}^{\mu}(\xi)=\langle n|(a_{\mu\nu}+a_{\nu\mu})\partial_{\xi_\nu}+\beta_\mu|m\rangle, \tag{2.24}$$
$$C_{nm}(\xi)=\langle n|a_{\mu\nu}\partial_{\xi_\mu}\partial_{\xi_\nu}+\beta_\mu\partial_{\xi_\mu}+\gamma|m\rangle,$$

and one can show that $B_{00}^{\mu}=0$ provided U_0 is real, which we shall assume. Using (2.10a), one can write

$$A_{00}^{\mu\nu}(\xi) = -\frac{1}{2\mu}\delta_{\mu\nu} - \frac{m}{2\mu^2}\overline{A}_{\mu\nu}(\xi)\,, \tag{2.25}$$

so that (2.23) can be written

$$\left(E - W_0 + \frac{1}{2\mu}\nabla^2 + \frac{m}{2\mu^2}\overline{A}_{\mu\nu}\partial_{\xi_\mu}\partial_{\xi_\nu} - C_{00}\right)F_0^{(+)}(\xi) = 0\,. \tag{2.26}$$

The term $\overline{A}_{\mu\nu}$ makes this an unconventional type of Schrödinger equation which can be converted to the conventional type (at least to order m/μ) by the coordinate transformation

$$\xi_\mu = \xi'_\mu[1 + (m/\mu)g(\xi'^2)]\,, \tag{2.27}$$

where we determine g by the condition that the second derivatives in (2.26) enter only as a Laplacian. In the new coordinate ξ', Eq. (2.26) becomes (we drop the primes now as a notational change)

$$\begin{aligned}\Big[E - W_0(\xi) - \frac{m}{\mu}g\xi\frac{\partial W_0}{\partial\xi} + \frac{1}{2\mu}\left(1 - \frac{2m}{\mu}g\right)\nabla^2 \\ - \frac{m}{2\mu^2}\big[(10g' + 4g''\xi^2)\vec{\xi}\cdot\vec{\nabla} + 4g'\vec{\xi}\vec{\xi}:\vec{\nabla}\vec{\nabla}\big] \\ + \frac{m}{2\mu^2}\overline{A}_{\mu\nu}\partial_{\xi_\mu}\partial_{\xi_\nu} - C_{00}\Big]F_0^{(+)} = 0\,.\end{aligned} \tag{2.28}$$

Since U_0 is a Σ state of the molecule, invariance arguments lead to the requirement that

$$\overline{A}_{\mu\nu}(\xi) = \delta_{\mu\nu}A_1(\xi^2) + \xi_\mu\xi_\nu A_2(\xi^2)\,, \tag{2.29}$$

where A_1 and A_2 are functions of ξ^2.

If we determine g by the condition

$$\delta_{\mu\nu}(A_1 - 2g) + \xi_\mu\xi_\nu A_2 - 4g'\xi_\mu\xi_\nu = \delta_{\mu\nu}\sigma(\xi^2)\,, \tag{2.30}$$

where σ is a new scalar function, we then obtain

$$g = -\frac{1}{4}\int_{\xi^2}^{\infty} dt\, A_2(t) \tag{2.31}$$

and

$$\sigma(\xi^2) = A_1(\xi^2) + \frac{1}{2}\int_{\xi^2}^{\infty} dt\, A^2(t)\,. \tag{2.32}$$

Then (2.28) can be rewritten

$$\begin{aligned}\Big[E - W_0 + \frac{1}{2\mu}\left(1 + \frac{m}{\mu}\sigma\right)\nabla^2 - \frac{m}{\mu}g\xi\frac{\partial W_0}{\partial\xi} \\ - \frac{m}{\mu^2}(5g' + 2\xi^2 g'')\vec{\xi}\cdot\vec{\nabla}_\xi - C_{00}\Big]F_0^{(+)} = 0\,.\end{aligned} \tag{2.33}$$

We may divide out the factor $1 + (m/\mu)\sigma$ to obtain (note $C_{00} \sim 1/\mu$) in order m/μ:

$$\begin{aligned}\Big(E - W_0 + \frac{1}{2\mu}\nabla^2 - \frac{m}{\mu}g\xi\frac{\partial W_0}{\partial\xi} - \frac{m}{\mu}\sigma(E - W_0) - C_{00} \\ - \frac{m}{\mu^2}(5g' + 2\xi^2 g'')\vec{\xi}\cdot\vec{\nabla}\Big)F_0^{(+)} = 0\,.\end{aligned} \tag{2.34}$$

The last term, a first derivative may be transformed away by the transformation

$$F_0 = \exp[(m/\mu)(\tfrac{3}{2}g + \xi^2 g')]\overline{F}_0\,, \tag{2.35}$$

which generates new potential terms of order m^2/μ^3, which we drop. Then, dropping the bar on F_0 we obtain the equation

$$\begin{aligned}\Big(E - W_0 + \frac{1}{2\mu}\nabla^2 - \frac{m}{\mu}g\xi\frac{\partial W_0}{\partial\xi} \\ - \frac{m}{\mu}\sigma(E - W_0) - C_{00}\Big)F_0^{(+)} = 0\,,\end{aligned} \tag{2.36}$$

where the energy-dependent potential is now explicitly shown. These terms were erroneously omitted in I. σ is given by (2.32) and $A_{1,2}$ can be obtained from (2.29), (2.25), (2.24), and (2.10a) with the result

$$\begin{aligned}A_1 = \tfrac{1}{2}\Sigma_i\langle 0|\vec{x}_i\cdot\vec{\nabla}_\xi f_i - \vec{x}_i\cdot\hat{\xi}\hat{\xi}\cdot\vec{\nabla}_\xi f_i \\ - \tfrac{1}{2}\lambda[\vec{\nabla}_i\cdot(\vec{x}_i f_i) - \hat{\xi}\cdot\nabla_i(\hat{\xi}\cdot\vec{x}_i f_i)] \\ + \tfrac{1}{2}(f_i^2 - 1) + \tfrac{1}{4}(\vec{x}_i\cdot\vec{\nabla}f_i^2 - \hat{\xi}\cdot\vec{x}_i\hat{\xi}\cdot\vec{\nabla}_i f_i^2) \\ + \tfrac{1}{4}[x_i^2 - (\hat{\xi}\cdot\vec{x}_i)^2(\vec{\nabla}_i f_i)^2]|0\rangle\,,\end{aligned} \tag{2.37a}$$

$$\begin{aligned}A_2 = (1/2\xi^2)\Sigma_i\langle 0|(3\hat{\xi}\cdot\vec{x}_i\hat{\xi}\cdot\vec{\nabla}_\xi - \vec{x}_i\cdot\vec{\nabla}_\xi)f_i \\ - \tfrac{1}{2}\lambda(3\hat{\xi}\cdot\vec{x}_i\hat{\xi}\cdot\vec{\nabla}_i - \vec{x}_i\cdot\vec{\nabla}_i)f_i \\ + \tfrac{1}{4}(3\hat{\xi}\cdot\vec{x}_i\hat{\xi}\cdot\vec{\nabla}_i - \vec{x}_i\cdot\vec{\nabla}_i)f_i^2 \\ + \tfrac{1}{4}[3(\hat{\xi}\cdot\vec{x}_i)^2 - x_i^2](\vec{\nabla}_i f_i)^2|0\rangle\,.\end{aligned} \tag{2.37b}$$

In order to explicitly exhibit the m/μ corrections in the scattering potential, W_0 and H_{ad} can be expanded in this parameter,

$$W_0 = W_0^{(0)} + (m/\mu)\langle 0|H_{\text{ad}}^{(1)}|0\rangle + \cdots\,. \tag{2.37c}$$

We then define

$$(m/\mu)\overline{C}_{00} = C_{00} + (m/\mu)\langle 0|H_{\text{ad}}^{(1)}|0\rangle\,; \tag{2.38}$$

and by using (2.24), (2.21), (2.20), and (2.9), we can obtain

$$(m/\mu)\overline{C}_{00} = (m/\mu)\langle 0|T^{(1)} + V^{(1)}|0\rangle\,, \tag{2.39}$$

where $T^{(1)}$ and $V^{(1)}$ are the first-order parts of T [Eq. (2.9)] and V [(Eq. (2.12)], respectively. In all the expectation values [(2.37c) and (2.39)], zero-order wave functions are used. These are the conventional wave functions calculated by molecular theorists except that the origin of the electron coordinates is here taken as the center of mass of the nuclei where in the usual calculation it is their midpoint. We now shift to these more usual coordinates,

$$\vec{y}_i = \vec{x}_i + \tfrac{1}{2}\lambda\vec{\xi}\,,\quad \vec{R} = \vec{\xi} \tag{2.40}$$

and define

$$U_0(X, \vec{\xi}) = u_0(Y, \vec{R})\,,\quad f(\vec{x}, \vec{\xi}) = \overline{f}(\vec{y}, \vec{R})\,. \tag{2.41}$$

The boundary conditions on $\bar{f}$ are then

$$\lim_{R\to\infty} \bar{f} \to \begin{cases} +1 & \text{for } \vec{y} \to \tfrac{1}{2}\vec{R} \\ -1 & \text{for } \vec{y} \to \tfrac{1}{2}\vec{R} \end{cases} \tag{2.42}$$

and we may take $\bar{f}$ as an odd function of both $\vec{y}$ and $\vec{R}$. In these new coordinates we obtain

$$\begin{aligned} A_1 = 2 \int d^3y\, \rho(\vec{y},\vec{R}) \{ & \tfrac{1}{2}(\bar{f}^2 - 1) + (\vec{y}\cdot\vec{\nabla}_R - \hat{R}\cdot\vec{y}\hat{R}\cdot\vec{\nabla}_R)\bar{f} \\ & + \tfrac{1}{4}(\vec{y}\cdot\vec{\nabla} - \hat{R}\cdot\vec{y}\hat{R}\cdot\vec{\nabla})\bar{f}^2 \\ & + \tfrac{1}{4}[y^2 - (\vec{y}\cdot\hat{R})^2]\,|\vec{\nabla}\bar{f}|^2 \}, \end{aligned} \tag{2.43a}$$

$$\begin{aligned} A_2 = \frac{2}{R^2} \int d^3y\, \rho(\vec{y},\vec{R}) \{ & (3\hat{R}\cdot\vec{y}\hat{R}\cdot\vec{\nabla}_R - \vec{y}\cdot\vec{\nabla}_R)\bar{f} \\ & + \tfrac{1}{4}(3\hat{R}\cdot\vec{y}\hat{R}\cdot\vec{\nabla} - \vec{y}\cdot\vec{\nabla})\bar{f}^2 \\ & + \tfrac{1}{4}[3(\hat{R}\cdot\vec{y})^2 - y^2 + \tfrac{1}{2}\lambda^2R^2]\,|\vec{\nabla}\bar{f}|^2 \}, \end{aligned} \tag{2.43b}$$

where $\rho(\vec{y},\vec{R})$ is the single-electron density in the state u_0. In these coordinates we also obtain

$$\begin{aligned} \langle 0|T^{(1)}|0\rangle = -(1/2m)\langle 0| & \nabla_R{}^2 - \tfrac{1}{4}(\Sigma_i\vec{\nabla}_i)^2 \\ & + \tfrac{1}{2}\Sigma_i[\vec{\nabla}_i^2, \vec{y}_{i\mu}\bar{f}_i]\nabla_{R_\mu} \\ & - \tfrac{1}{8}\lambda^2\Sigma_{ij}[\nabla_i{}^2, \bar{f}_i]\vec{R}\cdot\vec{\nabla}_j|0\rangle \end{aligned} \tag{2.44a}$$

and

$$\begin{aligned} \langle 0|V^{(1)}|0\rangle = \langle 0| - 2e^2\Sigma_i & \frac{\vec{y}_i - \frac{1}{2}\vec{R}}{|\vec{y}_i - \frac{1}{2}\vec{R}|^3} \\ & \cdot\{\vec{R} - \tfrac{1}{2}\lambda^2\vec{R}\Sigma_j\bar{f}_j - \Sigma_j\vec{y}_j[\tfrac{1}{2}(1+\bar{f}_j)]\} \\ & + 4e^2\left(-\frac{1}{R} + \frac{\vec{R}}{2R^3}\cdot\Sigma_i\vec{y}_i\bar{f}_i\right)|0\rangle \end{aligned} \tag{2.44b}$$

from which $\bar{C}_{00}$ [Eq. (2.39)] can be constructed.

Now let us return to the dispersive part of the potential

$$\mathcal{V}_{00} = \langle 0|H\frac{Q}{E^+ - QHQ}H|0\rangle = \langle 0|T_\xi\frac{Q}{E^+ - QHQ}T_\xi|0\rangle. \tag{2.45}$$

The operator T_ξ is already of order μ^{-1} so, as in I, the denominator may be treated to lowest order which makes it diagonal in the adiabatic states. Furthermore, the intermediate state Green's function is essentially local so that $\mathcal{V}$ takes the simple form

$$\mathcal{V}_{00} = \sum_{n\neq 0} \langle 0|T_\xi|n\rangle \frac{1}{W_0(\infty) - W_n(\xi)} \langle n|T_\xi|0\rangle. \tag{2.46}$$

Now, because of the fact that $T_\xi \sim 1/\mu$ then $\mathcal{V} \sim 1/\mu^2$. The only place where μ^{-2} has been kept is in $A^{\mu\nu}$ so that we need keep only terms $\sim\mu^{-2}$ which have two ξ derivatives acting on F. These are

$$\delta A_{00}^{\mu\nu} = \sum_{n\neq 0} \frac{B_{0n}^\mu B_{n0}^\nu}{W_0(\infty) - W_n(R)}, \tag{2.47}$$

which will be added to $A_{00}^{\mu\nu}$ in Eq. (2.23). From Eqs. (2.24) and (2.10), we may obtain B_{0n}^μ. In the new coordinates [Eq. (2.40)], we obtain

$$\begin{aligned} B_{0n}^\mu = & (1/\mu)\langle 0| - \nabla_{R_\mu} - \tfrac{1}{4}\Sigma_i[\nabla_i{}^2, y_{i\mu}\bar{f}_i]|n\rangle \\ & + (\lambda R_\mu/8\mu)\langle 0|\Sigma_i[\nabla_i{}^2, \bar{f}_i]|n\rangle, \end{aligned} \tag{2.48}$$

where the first (second) term survives only for intermediate states of even (odd) parity. Evaluation of the sum in (2.47) in a formidable task which we shall not attempt. However its contribution to $A_{00}^{\mu\nu}$ is likely to be small because of the large excitation energy associated with He. That is, the denominator in (2.47) is large even for the first excited state. We therefore drop $\delta A_{00}^{\mu\nu}$.

Then examination of Eq. (2.36) shows that the effective-scattering potential may be written

$$\begin{aligned} V_{\text{eff}}(R) = & W_0^0(R) - W_0^0(\infty) \\ & + \frac{m}{\mu}\left(\sigma[E - W_0^0(R)] + gR\frac{\partial W_0^0}{\partial R} + \bar{C}_{00} - W_0^1(\infty)\right), \end{aligned} \tag{2.49}$$

where the energy dependence is explicit and the mass dependence is explicit in the m/μ factor and implicitly in $\bar{C}_{00}$ and σ.

Another feature of the result is the appearance of the switching function in the m/μ correction to the potential. Since this function has so far been defined only by its boundary conditions [Eq. (2.42)] it is arbitrary in the rest of configuration space, and the potential [Eq. (2.49)] is therefore undetermined to this extent. We must therefore conclude that the scattering potential is not uniquely defined in the adiabatic representation, beyond the lowest order in m/μ. Physically, this nonuniqueness of the potential is the result of our forcing the nonlocal potential which results from the inclusion of the Pauli principle (for electrons) into a local form. This lack of uniqueness will however not be reflected in physical observables such as scattering data (see the Appendix).

Recently, the scattering potentials for $He_4 + He_4$ and $He_3 + He_3$ have been extracted from low-energy scattering data[2] with a marginal difference in the two potentials. Calculation of the two different effective potentials [Eq. (2.49)] is evidently a formidable task but a great simplification results from combining the two measurements. We note that for both cases $\lambda = 0$ so that we obtain

$$\frac{\mu_{44}[V_{\text{eff}}(R)]_{44} - \mu_{33}[V_{\text{eff}}(R)]_{33}}{\mu_{44} - \mu_{33}} = W_0(R) - W_0(\infty), \tag{2.50}$$

where V_{eff} are to be taken directly from experiment at a fixed energy and $W_0(R)$ is the zero-order calculated interaction. The requirement that $V_{\text{eff}}(R)$ be determined at a *fixed* energy is a restrictive one since this determination strictly speaking requires data at all energies.

We may estimate the order of magnitude of the energy-dependent term in Eq. (2.49), which is

$$(m/\mu)\sigma(R)[E-W_0^0(\infty)].$$

The factor σ will turn out to be positive and of the order unity near its maximum and $m/\mu \sim 3\times10^{-4}$. The experiment of Ref. 2 covers the energy range 0.01 to 1 eV so that this part of the potential is repulsive and ranges from about 3×10^{-6} to 3×10^{-4} eV at its maximum in configuration space. The zero-order potential $[W_0^0(R)-W_0^0(\infty)]$ has a magnitude of about 10^{-3} eV at its minimum so that the energy dependence of the potential is small compared to the potential throughout this energy range. However, it is not small compared to the difference in $(V_{\text{eff}})_{44}-(V_{\text{eff}})_{33}$ determined in Ref. 2. This difference is about 5×10^{-5} eV at the potential minimum, which is comparable to the magnitude of the energy-dependent part. Therefore, the energy dependence must be explicitly inserted before the potential difference can be extracted from the cross-section data.

III. DETERMINATION OF THE SWITCHING FUNCTION AND NUMERICAL RESULTS

If one uses the complete set of adiabatic functions U_n to expand the total wave function and solves the resulting coupled equations then the scattering data which is obtained must be exact and independent of our choice of $\bar{f}$. If, however, we choose a truncated basis set, then we expect that the results of the calculation will depend upon this choice. We can optimize some property of the scattering problem with this freedom. The one chosen here is the total cross section or equivalently the forward-scattering amplitude.

This is accomplished via the Kohn variational principal by requiring that the integral

$$I=\int d\tau\, \Psi^{(-)*}(E-H)\Psi^{(+)} \tag{3.1}$$

be stationary with respect to variations[7] of f subject to the boundary conditions [Eq. (2.42)]. For simplicity, we shall use only a single adiabatic state in $\Psi^{(\pm)}$,

$$\Psi^{(\pm)}=F^{(\pm)}(\vec{\xi})U_0(X,\vec{\xi}), \tag{3.2}$$

where we contemplate variations in $F^{(\pm)}$ and in f_i.

Variation of $F^{(-)*}(F^{(+)})$ yields an equation for $F^{(+)}(F^{(-)*})$, which is just Eq. (2.26). Variation of f_i is slightly more complex. We carry it out by assuming that the integral, Eq. (3.1), is written in terms of the original coordinates $\vec{R}_i$ and $\vec{r}_j$. The functions f_i then enter through the definition of ξ [Eq. (2.7)] and through the definition of U_0 by H_{ad} [Eq. (2.16)]. The appearance of $\vec{\xi}$ in F does not contribute to this variation since F is varied independently of f_i. Then the total variation due to the variation of f_i enters through U_0 and is

$$\delta_{\text{tot}}U_0=\delta\vec{\xi}\cdot\vec{\nabla}_\xi U_0+\delta U_0, \tag{3.3}$$

where the last term signifies the variation of U_0 with respect to f_i because of its appearance in H_{ad}. Using the transformation equations (2.3), one readily obtains

$$\delta\vec{\xi}=\frac{m}{2\mu}\Sigma_i\vec{x}_i\delta f_i \tag{3.4}$$

and δU_0 is given by

$$\delta U_0=\sum_{n\neq0}\frac{U_n\langle n|\Sigma_i\delta f_i(\partial H_{\text{ad}}/\partial f_i)|0\rangle}{W_0(\xi)-W_n(\xi)} \tag{3.5}$$

and we note that

$$\frac{\partial H_{\text{ad}}}{\partial f_i}\sim\frac{m}{\mu}.$$

An explicit calculation of the sum in (3.5) would be difficult but we drop δU_0 compared to the first term in (3.3) because of the large excitation energy of He. That is, the denominator in (3.5) is large even when n is the first excited state. The variation of (3.1) is then performed using only the first term of (3.3) and keeping U_0 real. After the variation the integral is written in the new coordinates:

$$\begin{aligned}0=\int(dX)d^3\xi J[&F^{(-)*}\delta U_0(E-W_0-T_\xi)U_0F^{(+)}\\&+F^{(-)*}U_0(E-W_0-T_\xi)\delta U_0F^{(+)}].\end{aligned} \tag{3.6}$$

We now exploit the Hermiticity of T_ξ and use the equation of motion for $F_0^{(\pm)}$ to get (to order $1/\mu$)

$$\begin{aligned}0=\int(dX)d^3\xi\Big\{&F^{(-)*}\delta U_0\Big[C_{00}U_0-\Big(-\frac{1}{2\mu}\nabla_\xi^2+\beta_\mu\partial_{\xi_\mu}+\gamma\Big)U_0\Big]F^{(+)}+F^{(+)}\delta U_0\Big[C_{00}U_0-\Big(-\frac{1}{2\mu}\nabla_\xi^2+\beta_\mu\partial_{\xi_\mu}+\gamma\Big)U_0\Big]F^{(-)*}\\&-F^{(-)*}\delta U_0\Big[\Big(\beta_\mu-\frac{1}{\mu}\partial_{\xi_\mu}\Big)U_0\Big]\partial_{\xi_\mu}F^{(+)}/-F^{(+)}\delta U_0\Big[\Big(\beta_\mu-\frac{1}{\mu}\partial_{\xi_\mu}\Big)U_0\Big]\partial_{\xi_\mu}F^{(-)*}\Big\}.\end{aligned} \tag{3.7}$$

Consider the last two terms first. They may be combined to give

$$-\delta U_0\left[\left(\beta_\mu-\frac{1}{\mu}\partial_{\xi_\mu}\right)U_0\right]\partial_{\xi_\mu}(F^{(+)}F^{(-)*}), \tag{3.8}$$

so that the derivates of $F^{(\pm)}$ which we would expect to be of order $P(R)$ (the local momentum) suffer strong cancellation. If the momentum is high enough for the eikonal[8] theory to describe the scattering then $\partial_\xi \sim 1/p$ in Eq. (3.8) rather than $\partial_\xi \sim p$. Thus, the first two terms of (3.7) can be expected to dominate. At extremely low energies $\partial_\xi \sim p$ in (3.8) and again the first terms in (3.7) dominate. We therefore drop the last two terms in (3.7) and write it

$$0=\int (dX)d^3\xi\,\delta U_0[\langle 0|O(X,\vec{\xi})|0\rangle - O(X,\vec{\xi})]U_0F^{(-)*}F^{(+)}, \tag{3.9}$$

where we have written

$$O(X,\vec{\xi})=-(1/2\mu)\nabla_\xi{}^2+\vec{\beta}\cdot\vec{\nabla}_\xi+\gamma \tag{3.10}$$

and

$$C_{00}(\xi)=\langle 0|O(X,\xi)|0\rangle. \tag{3.11}$$

Now we use Eqs. (3.3) and (3.4) and choose δf_i to be an arbitrary variation

$$\delta f_i(\vec{x},\vec{\xi})=\delta_{i1}\delta(\vec{x}-\vec{x}')\delta(\vec{\xi}-\vec{\xi}') \tag{3.12}$$

to get

$$0=\int d^3x_2\,d^3x_3\,d^3x_4\frac{m}{2\mu}\vec{x}_1\cdot\vec{\nabla}_\xi U_0 \times[\langle 0|O(X,\vec{\xi})|0\rangle - O(X,\vec{\xi})]U_0|_{x_1=x',\,\xi=\xi'}, \tag{3.13}$$

where we have been able to divide out $F^{(-)*}F^{(+)}$. Therefore, Eq. (3.13), which is the integro-differential equation determining $f(\vec{x}',\vec{\xi}')$ is dependent only on the properties of the bound state. That is, even though we have used a scattering criterion to specify the f_i the result (for most energies) is an equation which depends only on bound state properties. This says that if we could solve Eq. (3.13) for f_i we would optimize for scattering for a large group of scattering conditions.

It is clear that we shall not be able to solve (3.13). Examination of β and γ in Eqs. (2.10b) and (2.22), show that Eq. (3.13) is a nonlinear integro-differential equation for f_i. We can examine the behavior at large ξ in the reference configuration and find that f_i approaches its asymptotic value, ±1, as ξ^{-3} the coefficient is of the order of magnitude of the van der Waals interaction which is very small for He$_2$. Rather than try to solve (3.13) we shall construct a function which depends only on U_0 (as would the exact solution). We note that a form [in the coordinate system, Eq. (2.40)]

$$\bar{f}(\vec{y},\vec{R})=\frac{a_+(\vec{y},\vec{R})-a_-(\vec{y},\vec{R})}{a_+(\vec{y},\vec{R})+a_-(\vec{y},\vec{R})} \tag{3.14}$$

satisfies the boundary conditions provided that, in the limit $R\to\infty$,

$$a_-|_{\vec{y}=\vec{R}/2}=0,\quad a_+|_{\vec{y}=\vec{R}/2}\neq 0, \qquad a_+|_{\vec{y}=-\vec{R}/2}=0\quad a_-|_{\vec{y}=-\vec{R}/2}\neq 0. \tag{3.15}$$

If we define a single-particle density, then

$$\rho(\vec{y},\vec{R})=\int d^3y_2\,d^3y_3\,d^3y_4|u_0(\vec{y},\vec{y}_2,\vec{y}_3,\vec{y}_4;\vec{R})|^2, \tag{3.16}$$

and then in the limit $R\to\infty$,

$$\rho(\vec{y},\vec{R})=\frac{1}{2}\int d^3z\left[\left|\phi\left(\vec{y}-\frac{\vec{R}}{2},\vec{z}\right)\right|^2+\left|\phi\left(\vec{y}+\frac{\vec{R}}{2},\vec{z}\right)\right|^2\right], \tag{3.17}$$

where ϕ is the ground-state wave function of free atomic helium. Then defining

$$a_\pm(\vec{y},\vec{R})=\rho(\vec{y},\vec{R})-\frac{1}{2}\int d^3z\left|\phi\left(\vec{y}\pm\frac{\vec{R}}{2},\vec{z}\right)\right|^2, \tag{3.18}$$

we see that this satisfies Eq. (3.15) and therefore satisfies the boundary conditions on $\bar{f}$. The form (3.18) results in an $\bar{f}$ that approaches its asymptotic value as R^{-6} rather than R^{-3} as would a solution of Eq. (3.13). This may be rectified by calling Eq. (3.18) $a_\pm^2$ but in either case the error is proportional to the small van der Waals interaction and probably negligible.

If we use a Slater determinant for u_0 and another one for ϕ we may write $\bar{f}$ in terms of these orbitals as

$$\bar{f}(\vec{y},\vec{R})=\frac{\frac{1}{2}[g^2(\vec{y}-\frac{1}{2}\vec{R})-g^2(\vec{y}+\frac{1}{2}\vec{R})]}{u_g^2(\vec{y},\vec{R})+u_u^2(\vec{y},\vec{R})-\frac{1}{2}[g^2(\vec{y}-\frac{1}{2}\vec{R})+g^2(\vec{y}+\frac{1}{2}\vec{R})]}, \tag{3.19}$$

where g is the orbital of the helium atom and $u_{g,u}$ are the orbitals of the He$_2$ molecule.

The form (3.19) is, of course, only an approximate solution of (3.13) so that it does not seem worthwhile to use accurate wave functions for u_g, u_u, and ϕ. Instead we use the Hylleras function

$$g(x)=\frac{\alpha^{3/2}}{\pi^{1/2}}e^{-\alpha x},\quad \alpha=\tfrac{27}{16} \tag{3.20}$$

for the atomic helium orbital and a linear-combination-of-atomic-orbitals (LCAO) approximation for u_g and u_u with g as the atomic orbital

$$u_{g,u}=\frac{1}{[2(1\pm S)]^{1/2}}[g(\vec{y}+\tfrac{1}{2}\vec{R})\pm g(\vec{y}-\tfrac{1}{2}\vec{R})], \tag{3.21}$$

where the overlap integral S is given by

$$S(R)=e^{-\alpha R}[1+\alpha R+\tfrac{1}{3}(\alpha R)^2]. \tag{3.22}$$

With these approximations, we obtain

TABLE I. A_1 and A_2. In each case, the first column is obtained from the wave functions of Gilbert and Wahl, the second from LCAO wave functions.

R^2	A_1		A_2	
1.5	0.325	0.419	0.178	0.171
2.0	0.259	0.257	0.059	0.056
2.5	0.191	0.162	0.014	0.016
3.0	0.129	0.097	0.005	0.003

$$\bar{f}(\vec{y},\vec{R}) = \frac{(1-S^2)(1-e^{-2\alpha\eta})}{(1+S^2)(1+e^{-2\alpha\eta})-4Se^{-\alpha\eta}}, \qquad (3.23)$$

where

$$\eta = |\vec{y}+\tfrac{1}{2}\vec{R}| - |\vec{y}-\tfrac{1}{2}\vec{R}|. \qquad (3.24)$$

With this definition of $\bar{f}$ the energy-dependent part of the effective potential [Eq. (2.49)], which is

$$(m/\mu)\sigma[E - W_0^0(\infty)],$$

can be evaluated. σ is given by Eqs. (2.32) and (2.43). We choose a Hartree-Fock representation of the wave function u_0 so that the single particle density is given by

$$\rho(\vec{y},\vec{R}) = \tfrac{1}{2}[u_g^2(\vec{y},\vec{R}) + u_u^2(\vec{y},\vec{R})],$$

where $u_{g,u}$ are the gerade and ungerade molecular orbitals of He_2. They can be obtained from the analytic Hartree-Fock solutions of Gilbert and Wahl.[9] A double numerical integral must be performed for each value of R to obtain σ. Note that λ enters σ and C only as $\lambda^2 = \frac{1}{49}$ or 0 so that the mass asymmetry effect is small. We therefore set $\lambda = 0$ in all cases so that the only remaining mass dependence in the energy-dependent potential is the over-all factor m/μ.

We also obtain σ by using the simpler, but less accurate, approximation (3.21) for the molecular orbitals. The results for the two calculations of A_1 and A_2 are given in Table I for a few values of R. We see that the two calculations for A_2 agree well while those for A_1 do not disagree by more than about 25%. We therefore perform all subsequent calculations with the simple wave functions [Eq. (3.21)]. In Fig. 1 we show the factor σ vs R. It is positive and so results in a repulsive energy-dependent potential for scattering but an attractive potential for bound state problems. This will make for greater binding and make the He_2 bound state more likely. Clearly, this effect must be taken into account when extrapolation of scattering data (or virial coefficients) is made to negative energies. Note that our result for σ is of order unity around $R \sim a_0$ and falls off exponentially for large R. This falloff is due to our simple choice of molecular wave functions [Eq. (3.21)] and will be replaced by a power-law behavior when more accurate wave functions are used.

In Fig. 2, we have shown

$$V_{\rm eff}^{(1)} = gR\frac{\partial W_0^0}{\partial R} + \bar{C}_{00} - W_0^1(\infty), \qquad (3.25)$$

which is the energy-independent part of the m/μ correction to $V_{\rm eff}$. It is attractive for small R, becomes repulsive for $R > 1.14$, peaks at about $R = 1.4$ and then falls off almost exponentially. Again the exponential falloff is due to the simple choice of wave functions. It peaks where the zero order potential $W_0^0(R) - W_0^0(\infty)$ is strongly repulsive

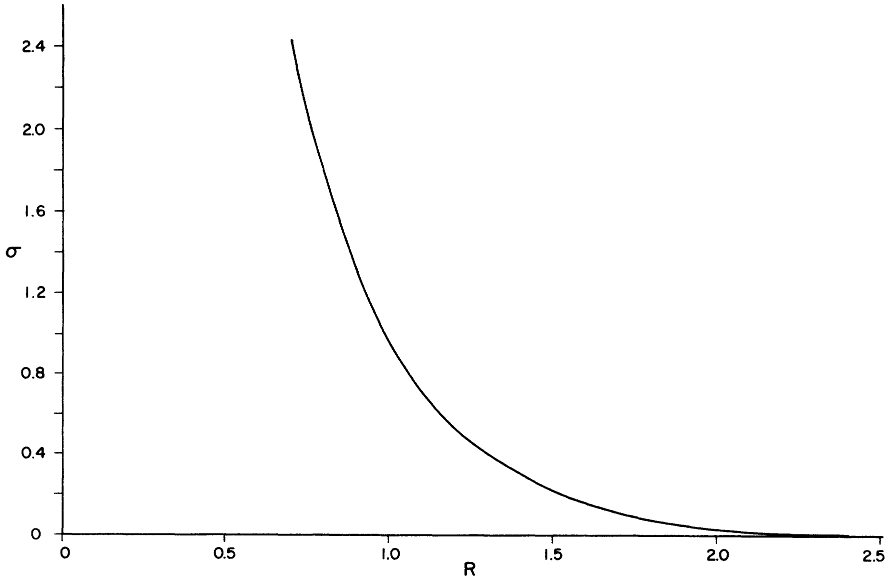

FIG. 1. σ vs R (Bohr radii).

and so represents only a small shift ($\sim m/\mu$) in this zero-order part where it is a few volts. It would be completely unobservable except for the fact that it enters as a mass-dependent term which can be isolated by comparing scattering by different isotopes.[2]

IV. COUPLED CHANNELS

There are circumstances where the approximation of the neglect of the dispersive potential is a poor one. The simplest of these is the case when another channel is strongly coupled to the elastic one. In that case a two-state expansion of Ψ is appropriate,

$$\Psi^{(\pm)} = U_0 F_0^{(\pm)} + U_1 F_1^{(\pm)} . \qquad (4.1$$

We may obtain exact coupled equations for these two scattering functions which will contain dispersive potentials. By hypothesis these will be negligible so that the resulting equation will be the matrix generalization of Eq. (2.23),

$$(E - W - A^{\mu\gamma}\partial_\mu\partial_\gamma - B^\mu\partial_\mu - C)\mathcal{T} = 0 \ , \qquad (4.2)$$

where $A^{\mu\gamma}$, B^μ, C, and W are now matrices in the space of channel number and $\mathcal{T}$ is the column matrix of scattering functions. (Note that W is diagonal and B^μ is off-diagonal.) We may proceed to remove the $\overline{A}^{\mu\gamma}$ term (2.25) by a generalization of (2.27),

$$\xi_\mu = [I + (m/\mu) g(\xi'^2)]\xi'_\mu , \qquad (4.3)$$

in which I is the unit matrix and g is an arbitrary matrix to be determined below. Since g will vanish at $\xi' \to \infty$ there is no difficulty in the physical interpretation of this transformation. Again we shall assume that the states are all Σ states so that the matrix generalizations of Eqs. (2.29)–(2.36) still apply. (The B^μ term is not zero here.) The result is

$$\biggl(E - W + \frac{1}{2\mu}\nabla^2 - \frac{m}{\mu}\sigma(E - W) - \frac{m}{\mu} g R \frac{\partial W}{\partial R} - C - B^\mu \partial_{\xi_\mu}\biggr)\mathcal{T} = 0 , \qquad (4.4)$$

which we write as

$$\left(\frac{P^2}{2\mu} + \frac{1}{2\mu}\nabla^2 - V_{\rm eff} - B^\mu\partial_{\xi_\mu}\right)\mathcal{T} = 0 . \qquad (4.5)$$

We shall concentrate on the coupling terms in (4.5) which are the off-diagonal elements of $V_{\rm eff}$ and $B^\mu\partial_\xi$. The off-diagonal elements of $V_{\rm eff}$ are

$$(V_{\rm eff})_{nm} = \frac{m}{\mu}\left[\sigma_{nm}E - [\sigma W^{(0)}(R)]_{nm} + C_{nm} + R\left(g\frac{\partial W^{(0)}}{\partial R}\right)_{nm}\right] , \qquad (4.6)$$

where C is given by (2.24),

$$C_{nm} = \langle n| - (1/2\mu)\nabla_R^2 + \beta_\mu\partial_{\xi_\mu} + \gamma |m\rangle . \qquad (4.7)$$

It may be shown that both σ and g vanish as $R \to \infty$ and so does C. The coupling terms in (4.5) are of two types: The $B^\mu\partial_{\xi_\mu}$ term depends on the local motion of the colliding particle and vanishes when they are not moving. The $V_{\rm eff}$ term does not have this property and so generates transitions even

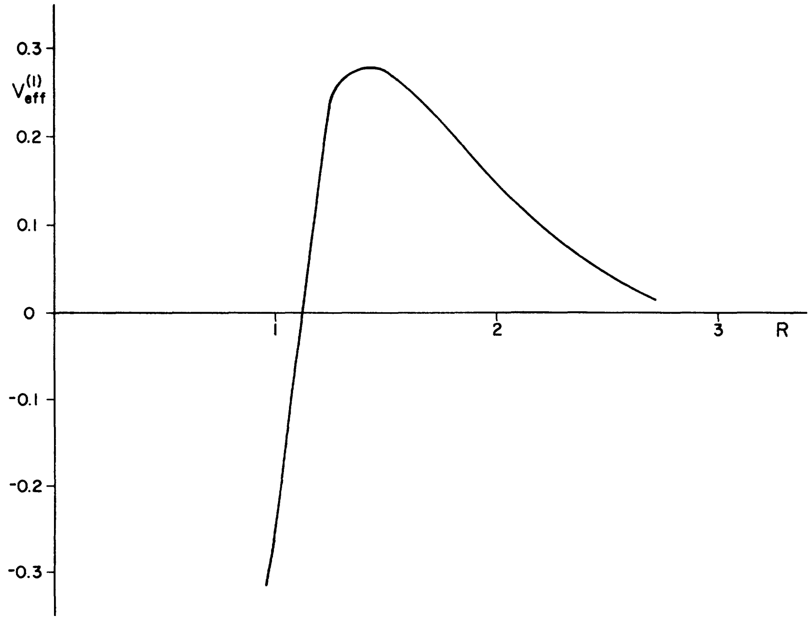

FIG. 2. $V_{\rm eff}^{(1)}$ (in Ry) vs R (Bohr radii).

when the colliding particles have no relative velocity. This means that we have transitions of order m/μ among adiabatic states even with no relative motion. This is not a property of our formulation alone. In the conventional formulation all the terms in Eq. (4.6) are absent except the ∇_R^2 term in C. This does not vanish for $R\rightarrow\infty$. In our formulation V_{eff} does vanish in this limit. Therefore, we may redefine our basis set u_n (in this case just two states) to diagonalize away the off diagonal elements of the operator $Z(\vec{y},\vec{R})$ whose matrix element is Eq. (4.6). These new states will still have the first property we require of adiabatic states, that is, they dissociate into an antisymmetric product of separated atomic wave functions, since $[V_{\text{eff}}(R)]_{nm}$ vanishes for $R\rightarrow\infty$. As we have pointed out V_{eff} does not vanish in the conventional formulation and so the states which diagonalize it do not have the correct dissociation property and can not be properly called adiabatic functions.

The operator Z contains $\vec{\nabla}_R$ so that its treatment for a complete set would in effect introduce $\vec{\nabla}_R$ terms into H_{ad}. This violates the second requirement for H_{ad}. Therefore, it is not possible to construct a complete set which has no adiabatic transitions in this order of m/μ.

The remaining coupling operator is $\vec{B}\cdot\vec{\nabla}_R$, where B^{μ}_{nm} is given by

$$B^{\mu}_{nm}=-(1/\mu)\langle n|\nabla_{R_{\mu}}+\tfrac{1}{4}\Sigma_i[\nabla_i^2,y_{i\mu}\bar{f}_i]|m\rangle$$
$$+(\lambda R_{\mu}/8\mu)\langle n|\Sigma_i[\nabla_i^2,\bar{f}_i]|m\rangle\,. \tag{4.8}$$

The first term survives when n and m are states of similar parity, the second for states of *opposite parity*. The usual formulation has only the ∇_R term of (4.8) as the coupling operator. This has spurious long-range behavior which is canceled by the inclusion of the remaining terms in (4.8). The identity

$$\Sigma_i[\nabla_i^2,y_{i\mu}\bar{f}_i]=\Sigma_{ij}[\nabla_i^2,y_{j\mu}\bar{f}_j]=-2m[H^{(0)}_{\text{ad}},\Sigma_{ij}y_{j\mu}\bar{f}_j] \tag{4.9}$$

and a similar one for the second term in (4.8), allows the simplification

$$B^{\mu}_{nm}=-(1/\mu)\langle n|\nabla_{R_{\mu}}+\tfrac{1}{2}m[W^{(0)}_m(R)-W^{(0)}_n(R)]$$
$$\times\Sigma_i y_{i\mu}\bar{f}_i|m\rangle+(\lambda/4\mu)R_{\mu}m$$
$$\times[W^{(0)}_m(R)-W^{(0)}_n(R)]\langle n|\Sigma_i\bar{f}_i|m\rangle\,. \tag{4.10}$$

The Landau-Zener formula is just the transition rate obtained by an approximate solution of the coupled equations[10] [Eq. (4.4)] in the special circumstance in which there is a close avoided (linear) crossing of the two levels. An important element in that formula is the coupling operator which is (4.10) instead of just its first term. The usual Landau-Zener transition probability from state 0 to state 1 can be written

$$P=e^{-2G_{\text{LZ}}} \tag{4.11}$$

where

$$G_{\text{LZ}}=\frac{\pi}{8}\frac{W^{(0)}_{10}}{|\Delta_{10}|}\bigg|_{R=R_c} \tag{4.12}$$

and where

$$W^{(0)}_{10}=W^{(0)}_1(R)-W^{(0)}_0(R)\,,$$
$$\Delta_{10}=\vec{v}(R)\cdot\langle 1|\vec{\nabla}_R|0\rangle\,. \tag{4.13}$$

$\vec{v}(R)$ is the local collision velocity and R_c is the nuclear separation at which $W^{(0)}_{10}$ is a minimum. This result is obtained from a solution of equations in which only the first term of B^{μ}_{10} is kept as a coupling operator. Inclusion of the correct form of B^{μ}_{10} modifies G in the Landau-Zener formula giving

$$G'=\frac{\pi}{8}\frac{W^{(0)}_{10}}{|\Delta'_{10}|}\bigg|_{R=R_c}, \tag{4.14}$$

where (for parity preserving collisions)

$$\Delta'_{10}=\vec{v}(R)\cdot\langle 1|\vec{\nabla}_R|0\rangle+\tfrac{1}{2}mW^{(0)}_{10}\vec{v}\cdot\langle 1|\Sigma_i\vec{y}_i\bar{f}_i|0\rangle\,. \tag{4.15}$$

If we estimate $\langle 1|\vec{\nabla}_R|0\rangle\sim a_0^{-1}$ and $\langle 1|\Sigma\vec{y}_i\bar{f}_i|0\rangle|_{R_c}\sim R_c$ then the second term is small provided that

$$W^{(0)}_{10}<1/ma_0R_c\,, \tag{4.16}$$

which is frequently the case. In that case we obtain

$$G'=G_{\text{LZ}}+\delta G\,, \tag{4.17}$$

where for Σ states, for example,

$$\delta G\doteq-G_{\text{LZ}}\tfrac{1}{2}mW^{(0)}_{10}\,\frac{\langle 1|\Sigma_i\vec{y}_i\cdot\hat{R}\bar{f}_i|0\rangle}{\langle 1|(\partial/\partial R)|0\rangle}\bigg|_{R=R_c}. \tag{4.18}$$

Even when the inequality (4.16) is satisfied, this may be non-negligible since G_{LZ} is frequently large and δG enters exponentially [Eq. (4.11)].

V. REARRANGEMENT COLLISIONS

We will complete our formal development of the subject by constructing the formalism describing a collision in which an electron is exchanged. As an example we use the collision

$$\text{H}+\text{He}\rightarrow\text{H}^-+\text{He}^+\,. \tag{5.1}$$

The scattering coordinate $\vec{\xi}$ is constructed by a method analogous to that used in Sec. II. We define the new coordinates from the old ones by

$$\vec{R}_1=\vec{\rho}-\frac{m}{M_1}\Sigma_i\vec{x}_i\left(\frac{1+f_i}{2}\right)+\frac{1}{M_1}\frac{\vec{\xi}}{\Delta},$$

$$\vec{R}_2=\vec{\rho}-\frac{m}{M_2}\Sigma_i\vec{x}_i\left(\frac{1-f_i}{2}\right)-\frac{1}{M_2}\frac{\vec{\xi}}{\Delta}, \qquad (5.2)$$

$$\vec{r}_i=\vec{\rho}+\vec{x}_i\,,$$

where the subscript 1(2) on R and M refers to the hydrogen (helium) nucleus, the function Δ is

$$\Delta=\left[\left(\frac{1}{M_1+m}+\frac{1}{M_2+2m}\right)\left(\frac{1-F}{2}\right)+\left(\frac{1}{M_1+2m}+\frac{1}{M_2+m}\right)\left(\frac{1+F}{2}\right)\right], \qquad (5.3)$$

and

$$F=\Sigma_i f_i\,. \qquad (5.4)$$

The boundary conditions are

$$\lim_{\xi\to\infty} f(\vec{x},\vec{\xi})=\begin{cases}+1 & \text{for } \vec{x}\to\vec{\xi}\left(\dfrac{M_1+m}{M_T}\right) \\ & \text{or } \vec{\xi}\left(\dfrac{M_1+2m}{M_T}\right) \\ -1 & \text{for } \vec{x}\to-\vec{\xi}\left(\dfrac{M_2+2m}{M_T}\right) \\ & \text{or } -\vec{\xi}\left(\dfrac{M_2+m}{M_T}\right),\end{cases} \qquad (5.5)$$

where $M_T=M_1+M_2+3m$. The terms $\frac{1}{2}(1\pm F)$ occurring in Δ are, in the $\xi\to\infty$ limit, projection operators onto the final and initial states of the reaction [Eq. (5.1)]. We see then that Δ^{-1} changes from the reduced mass of the neutral atoms to the reduced mass of the ions as F changes from -1 to $+1$ and so in each case, (5.2) goes over into the form of (2.3).

The implicit inverse of (5.2) is

$$\vec{\rho}=(M_1\vec{R}_1+M_2\vec{R}_2+m\Sigma_i\vec{r}_i)/M_T\,,\quad \vec{x}_i=\vec{r}_i-\vec{\rho}\,,$$

$$\vec{\xi}=M_2\left[\frac{1}{M_2+m}\left(\frac{1+F}{2}\right)+\frac{1}{M_2+2m}\left(\frac{1-F}{2}\right)\right]\left\{\vec{\rho}\left[1-\frac{m}{M_2}\left(\frac{3-F}{2}\right)\right]-\vec{R}_2-\frac{m}{M_2}\Sigma_i\vec{r}_i\left(\frac{1-f_i}{2}\right)\right\}$$
$$-M_1\left[\frac{1}{M_1+2m}\left(\frac{1+F}{2}\right)+\frac{1}{M_1+m}\left(\frac{1+F}{2}\right)\right]\left\{\vec{\rho}\left[1-\frac{m}{M_1}\left(\frac{3+F}{2}\right)\right]-\vec{R}_1-\frac{m}{M_1}\Sigma_i\vec{r}_i\left(\frac{1+f_i}{2}\right)\right\}. \qquad (5.6)$$

In the appropriate limit [see (5.5)], ξ goes over into the coordinate between the centers of mass of the separated atoms or ions. We may now define an adiabatic Hamiltonian with the aid of the "projection operators" $\frac{1}{2}(1\pm F)$ which has the correct dissociation properties in either channel of (5.1). We shall not do so here since the definition will not affect the only result which we will quote here which is the coupling operator which connects the channels of (5.1). This is

$$-(1/\mu)\langle 1\,|\vec{\nabla}_\xi-\tfrac{1}{4}\Sigma_j[\nabla_j^{2},(f_j-\lambda_0)(\vec{x}_j-\lambda_0\vec{\xi})]\,|2\rangle\cdot\vec{\nabla}_\xi\,,$$

where the states have been numbered 1, 2 and where λ_0 has the same meaning as in Sec. II. The remarks made at the end of Sec. IV apply equally well here.

The switching function in this case involves the mass ratio, m/M_T, through the boundary conditions (5.5). It is quite easy to construct a function similar to (3.19) which will satisfy these boundary conditions but it will contain the mass ratio. Since we are always interested in the lowest-order terms in m/M_T, where f_i enters we will eventually set $m/M_T=0$ in f_i in which case f_i will return to exactly the form (3.19).

VI. SUMMARY

We have generalized and simplified a previous treatment of atom-atom scattering to allow for dissimilar atoms. We made an expansion of the total wave function in adiabatic states and obtained a set of coupled equations describing scattering in the various channels. We found that the definition of an appropriate scattering coordinate which is symmetric in all electrons requires a nonlinear coordinate transformation which requires the introduction of the switching function. The same function is required for the definition of the adiabatic Hamiltonian. The criteria for H_{ad} are (i) in the limit of well-separated atoms H_{ad} becomes just the sum of two noninteracting atomic Hamiltonians; H_{ad} is symmetric in all electrons; (ii) the scattering coordinate appears only parametrically in H_{ad}. With these restrictions we found that it is impossible to construct a complete set of adiabatic states since there are transitions between states even when the atoms are not moving. However we did find that a limited set could be found which had no such transitions.

We found that the elastic-scattering potential was energy dependent in order m/μ and that it depended on the switching function. Since the switching function is not uniquely determined this means that the potential is also not uniquely determined. We can also view the switching function as an additional variational parameter. In that case it can be used to optimize some scattering property. We did this and roughly determined the switching function and the scattering potential.

The coupling operator between channels is also determined. It is found to depend on the switching function and to contain additional terms of the same order in m/μ as the one usually kept. This modifies formulas such as the Landau-Zener transition formula. It also allows coupling between states such as states of opposite parity in $H+D$ scattering. This will be investigated subsequently.

APPENDIX

The switching function is introduced in two ways here. The first is through the coordinate transformation [Eq. (2.7)] and the second through the definition of the adiabatic Hamiltonian which is basically just a prescription for breaking the total Hamiltonian into two different parts [Eq. (2.20)]. Neither of these can affect any of the physical observables, in particular, the scattering amplitude.

If there is some parameter ϵ in which the amplitude is expandable and if we choose the switching functions to be independent of this parameter then the amplitude must be independent of the details of the switching function in each order of ϵ. We have expanded the effective potential (which is not an observable) in powers of m/μ so it is tempting to also expand the amplitude in this parameter to exploit this invariance. However, the appearance of μ^{-1} as a coefficient of the highest derivative in (2.24) immediately indicates that the amplitude will not be expandable in m/μ. We have not yet been able to exploit this invariance in any other way.

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[1] Marvin H. Mittleman, Phys. Rev. 188, 221 (1969), hereafter referred to as I.

[2] Such dependence has recently been found experimentally. H. G. Bennewitz, H. Busse, H. D. Dohmann, D. E. Oates, and W. Schrades, Phys. Rev. Lett. 29, 533 (1972).

[3] This idea for this function was originally introduced by A. Russek and S. B. Schneiderman, Phys. Rev. 181, 311 (1969).

[4] The ideas described here are presented more fully in Ref. 1.

[5] In Ref. 1 a more complicated form of V was used. The complication is unnecessary.

[6] H. Feshbach, Ann. Phys. (N.Y.) 19, 287 (1962).

[7] The switching function has been introduced in two different ways: through the scattering coordinate and through the adiabatic Hamiltonian. It could be taken as two different functions but we have found no advantage in doing so.

[8] See, for example, J.C.Y. Chen and K. M. Watson, Phys. Rev. 174, 152 (1968).

[9] T. L. Gilbert and A. C. Wahl, J. Chem. Phys. 47, 3425 (1967). We would like to express our gratitude to Dr. Wahl for making unpublished wave functions of He_2 available to us.

[10] See, for example, K. M. Watson, in *Properties of Matter Under Unusual Conditions*, edited by H. Mark and S. Fernbach (Wiley, New York, 1968).