[*] Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

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[9] Inclusion of the p-state radiative widths gives a small $\sin\omega' t$ term which, when added to the $\cos\omega' t$ term, produces a small phase shift. The shift is less than 5 deg for the present case and is beyond our measurement accuracy. It should be stressed that for cases when $\gamma_i \sim \omega_i$ this phase shift may be substantial, and that the energy splitting calculated with neglect of γ_i (as in time-independent perturbation theory) will be seriously in error.

[10] The $p_{1/2}$-state decay rate is sufficiently close to the $p_{3/2}$ rate that their difference can be neglected in the fitting procedure.

[11] It should be noted that Bickel used an electrostatic field rather than a motional $\vec{v}\times\vec{B}$ field. No consequential difference should occur except that a foil may be placed within a magnetic field without perturbing the resulting motional electric field.

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Accurate Low-Energy Atom-Atom Scattering

Marvin H. Mittleman
The City College of the City University of New York, New York, New York 10031

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Measurements of low-temperature thermodynamic properties of gases yield information concerning the pairwise scattering parameters of the atoms of the gas. For recent helium-gas experiments, the He-He scattering potential has been determined with a high degree of accuracy. This necessitates a reanalysis of low-energy He-He scattering theory with inclusion of previously neglected effects of order m/M. The formulation requires a nonlinear transformation of coordinates to ensure the correct form of the incident wave, and a novel definition of the adiabatic Hamiltonian to ensure the dissociation of the "molecular" states into correct atomic states. In addition to the usual nonadiabatic terms, we find additional terms of the same order not usually encountered. They are necessary to make the potentials vanish at infinity. It is shown that the procedure of determining a potential interaction from the second virial coefficient (scattering data) and then predicting bound-state properties (if any) is a correct one.

I. INTRODUCTION

Measurement of thermodynamic functions as a function of temperature can yield extremely accurate information concerning the low-energy scattering parameters of the atoms of the gas. For example, the second virial coefficient can be related to the bound states and phase shift of the pairwise scattering of the atoms.[1] This analysis is based on a treatment of the atoms as structureless particles interacting through a local-energy-independent potential. Various potentials have been used to calculate the second virial coefficient in helium with the result that only potentials lying in a very narrow range will reproduce the experimental data. Typically, the uncertainty in the potential (near the minimum) is quoted at about 10^{-3}–10^{-4} eV^2. This accuracy is well beyond the usual situation encountered in atomic scattering phenomena so that a reanalysis of the atom-atom scattering event is necessary to take into account small effects previously neglected.

We shall pursue the scattering aspect of the problem here. It is clear that at the energies in question (10–300°K or 0.001–0.025 eV), the adiabatic [Born-Oppenheimer(BO)] representation of the wave function is a good one. It is also well known that this approximation introduces errors of order $(m/M)^{1/2}$, where m is the electron mass and M some relevant nuclear mass. These are usually negligible, but not in this case. The scattering problem must then be investigated in the adiabatic representation with the inclusion of these effects. A scattering potential will be derived which is, of course, energy-dependent and nonlocal. Another interesting question which arises is the relevance of this potential to the bound state He_2. The local-energy-independent potentials obtained phenomenologically from the virial coefficient data have been used to obtain conclusions concerning the existence of such a bound state.[2] The validity of such a procedure is certainly open to question when effects of order $(m/M)^{1/2}$ are relevant.

In Sec. II, the scattering problem is formulated keeping terms of relative order $(m/M)^2$. New nonadiabatic couplings are found which are of the same order as the usual terms. An equivalent potential for scattering is determined. It is found to be energy-independent and local in the order $(m/M)^2$ retained here. Finally, in Sec. III, it is shown that the same potential is relevant to the bound-state problem, so that the phenomenological procedures used are found to be correct.

II. SCATTERING PROBLEM

We deal explicitly with He-He scattering here, but the generalization to general A-A scattering is straightforward. The object of the formulation is to make an expansion of the total wave function Ψ, in adiabatic states $U_n(X, \vec{\xi})$, of the form

$$\Psi = \sum_n U_n(X, \vec{\xi}) F_n(\vec{\xi}) \quad . \tag{2.1}$$

Here, X represents all the electronic coordinates, and $\vec{\xi}$ is a scattering coordinate. The statement that U_n are adiabatic states means that $\vec{\xi}$ enters them only as a parameter and not as a dynamic coordinate. We demand that the scattering functions F_n have simple boundary conditions so that the incident wave is described by

$$F_n(\vec{\xi}) \sim \delta_{n0} e^{i\vec{p}\cdot\vec{\xi}} \quad , \quad \text{as} \quad \xi \to \infty \quad , \tag{2.2}$$

where 0 is the initial state of the atoms. We also require that the Pauli principle be satisfied for the electrons. This last requires that all the electron coordinates enter symmetrically.

Two complications beyond the usual theory are contained in these requirements. First, (2.2) means that the adiabatic states U_n must dissociate (for $\xi \to \infty$) into true atomic states – that is, the correct reduced mass must appear in the adiabatic Hamiltonian.[3] The Pauli principle, coupled with (2.2), also introduces a complication when high accuracy is required. For example, the ground adiabatic state in the limit $\xi \to \infty$ can dissociate into various configurations depending upon which electron is associated with which nucleus. One such configuration, which we refer to as the reference configuration is

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

where electrons $\vec{r}_1$ and $\vec{r}_2$ are bound to nucleus $\vec{R}_1$, etc. The relative coordinate between the c.m. of the two atoms is, in this configuration,

$$\vec{\xi} = [M\vec{R}_1 + m(\vec{r}_1 + \vec{r}_2)]/M_T - [M\vec{R}_2 + m(\vec{r}_3 + \vec{r}_4)]/M_T \quad , \tag{2.3}$$

where $M_T = M + 2m$.

Obviously, the electrons do not enter symmetrically and ξ will change in other configurations. This problem has been investigated previously by Thorson[4] and others[5] and very little new will be added to their formulations here.

The construction of an adiabatic Hamiltonian whose eigenfunctions satisfy the Pauli principle and dissociate into the correct free atoms is the first problem we turn to here.

Consider the reference configuration $(\vec{R}_1\vec{r}_1\vec{r}_2) \times (\vec{R}_2\vec{r}_3\vec{r}_4)$ and – at the beginning – only a single atom. Its Hamiltonian is

$$\begin{aligned} H^I &= T^I + V^I \quad , \\ T^I &= -\frac{1}{2M}\nabla^2_{R_1} - \frac{1}{2m}(\nabla^2_{r_1} + \nabla^2_{r_2}) \, , \\ V^I &= e^2\left(\frac{1}{\vec{r}_1} - \frac{2}{|\vec{r}_2 - \vec{R}_1|} - \frac{2}{|\vec{r}_2 - \vec{R}_1|}\right) . \end{aligned} \tag{2.4}$$

A more useful coordinate system is the c.m. coordinate and relative coordinates centered about a fixed position $\frac{1}{2}\vec{\xi}$.

$$\begin{aligned} \vec{\rho}_1 &= M_T^{-1}[M\vec{R}_1 + m(\vec{r}_1 + \vec{r}_2)] \quad , \\ \vec{x}_i &= \vec{r}_i - \vec{\rho}_1 + \tfrac{1}{2}\vec{\xi} \, ; \quad i = 1, 2 \quad . \end{aligned} \tag{2.5}$$

The Hamiltonian then becomes

$$\begin{aligned} H^I = &-\frac{1}{2M_T}\nabla_{\rho_1}{}^2 - \frac{1}{2}\left(\frac{1}{m} - \frac{1}{M_T}\right)\sum_{i=1}^{2}\nabla_i{}^2 \\ &+ \frac{1}{M_T}\nabla_1\cdot\nabla_2 + e^2\left(\frac{1}{x_{12}} - 2\sum_{i=1}^{2}\left|\vec{x}_i - \tfrac{1}{2}\vec{\xi} + \frac{m}{M}(\vec{x}_1 + \vec{x}_2 - \vec{\xi})\right|^{-1}\right), \end{aligned} \tag{2.6}$$

with eigenfunctions

$$\chi_{pn} = e^{i\vec{\mathrm{p}}\cdot\vec{\rho}_1}\varphi_n(\vec{\mathrm{x}}_1 - \tfrac{1}{2}\vec{\xi}, \vec{\mathrm{x}}_2 - \tfrac{1}{2}\vec{\xi}) \; . \qquad (2.7)$$

The Hamiltonian describing two noninteracting fixed atoms in the reference configuration, whose centers of mass are at $\frac{1}{2}\vec{\xi}$ and $-\frac{1}{2}\vec{\xi}$, is then

$$\begin{aligned}\mathcal{H} = &-\tfrac{1}{2}\left(\frac{1}{m} \cdot \frac{1}{M_T}\right)\sum_{i=1}^{4} \nabla_i^{\,2} \\ &+\frac{1}{M_T}(\nabla_1 \circ \nabla_2 + \nabla_3 \circ \nabla_4) + e^2\left(\frac{1}{x_{12}} + \frac{1}{x_{34}}\right) \\ &-2e^2 \sum_{i=1,2} \left|\vec{\mathrm{x}}_i - \tfrac{1}{2}\vec{\xi} + \frac{m}{M}(\vec{\mathrm{x}}_1 + \vec{\mathrm{x}}_2 - \vec{\xi})\right|^{-1} \\ &-2e^2 \sum_{i=3,4} \left|\vec{\mathrm{x}}_i + \tfrac{1}{2}\vec{\xi} + \frac{m}{M}(\vec{\mathrm{x}}_3 + \vec{\mathrm{x}}_4 + \vec{\xi})\right|^{-1} \; . \end{aligned} \qquad (2.8)$$

The operator is not symmetric in the electrons. We must generalize it so that it is, but yet reduces to the form (2.8) when operating on two well-separated atoms in the reference configuration.

In order to do this, we define an auxiliary function[5] $f_i = f(\vec{x}_i, \vec{\xi})$ such that in the limit $\xi \rightarrow \infty$

$$\begin{aligned} f_i &\rightarrow +1, \quad \text{for } \vec{\mathrm{x}}_i \rightarrow \tfrac{1}{2}\vec{\xi} \\ &\rightarrow -1, \quad \text{for } \vec{\mathrm{x}}_i \rightarrow \tfrac{1}{2}\vec{\xi} \; . \end{aligned} \qquad (2.9)$$

The function will be specified further below. The kinetic-energy terms can now be generalized to the symmetric Hermitian operator

$$\nabla_1 \circ \nabla_2 + \nabla_3 \circ \nabla_4 \rightarrow \frac{1}{4}\sum_{i<j=1}^{4}(1 + f_i f_j)\nabla_i \circ \nabla_j (1 + f_i f_j) \; ,$$

which has the correct properties for two well-separated atoms. The first term in the potential energy is readily generalized by

$$\frac{1}{x_{12}} + \frac{1}{x_{34}} \rightarrow \sum_{i<j=1}^{4} \frac{1}{x_{ij}} \; .$$

The additional terms vanish in the limit of well-separated atoms in the reference configuration. The last terms of (2.8) are somewhat more difficult to generalize. However, this can again be done with the aid of the functions f_i. One such generalization is

$$-2e^2\sum_{i=1}^{4}\left(|\vec{\mathrm{x}}_i - \tfrac{1}{2}\vec{\xi} + \vec{\Lambda}_i|^{-1} + |\vec{\mathrm{x}}_i + \tfrac{1}{2}\vec{\xi} + \vec{\Lambda}_i|^{-1}\right) \; ,$$

$$\text{where} \quad \vec{\Lambda}_i = \frac{m}{M}\sum_{j=1}^{4}[\tfrac{1}{2}(1 + f_i f_j)](\vec{\mathrm{x}}_j - \tfrac{1}{2}f_j\vec{\xi}) \; . \qquad (2.10)$$

This is, of course, symmetric in all electrons, and some simple algebra shows that it reduces to the last two terms in (2.8) when operating on the reference configuration. These results may be combined to yield an adiabatic Hamiltonian

$$\begin{aligned} H_{\mathrm{ad}} = &-\frac{1}{2}\left(\frac{1}{m} - \frac{1}{M_T}\right)\sum_{i=1}^{4}\nabla_i^{\,2} + \frac{1}{4M_T}\sum_{i>j=1}^{4} \\ &\times(1 + f_i f_j)\nabla_i \cdot \nabla_j (1 + f_i f_j) \\ &+ e^2 \sum_{i>j=1}^{4}\frac{1}{x_{ij}} - 2e^2\sum_{i=1}^{4}\left(|\vec{\mathrm{x}}_i - \tfrac{1}{2}\vec{\xi} + \vec{\Lambda}_i|^{-1}\right. \\ &\left. + |\vec{\mathrm{x}}_i + \tfrac{1}{2}\vec{\xi} + \vec{\Lambda}_i|^{-1}\right) + e^2/|\vec{\xi} + 2\vec{\Lambda}| \; , \end{aligned} \qquad (2.11)$$

which is an even function of $\vec{\xi}$ provided only that $f_i(\vec{\xi}) = -f_i(-\vec{\xi})$, a condition which we shall impose. We take this Hamiltonian as a generalization of the usual adiabatic one and note that they become identical in the limit $m/M = 0$. The last term is just e^2/R_{12} written in coordinates defined below [see (2.13) and (2.18)]. It is included here for convenience. We define a complete set of adiabatic states by

$$[W_n(\xi) - H_{\mathrm{ad}}(X, \vec{\xi})]\, U_n(X, \vec{\xi}) = 0 \; , \qquad (2.12)$$

which depend parametrically upon $\vec{\xi}$ which will be identified as the scattering coordinate. Note that by construction, in the limit $\xi \rightarrow \infty$, the lowest states U_n separate into two atomic states whose centers of mass are separated by $\vec{\xi}$. All electrons enter symmetrically. It is, in principle, a simple task to get these eigenfunctions and eigenvalues as a power series in (m/M) if the usual BO wave functions are known.

Now we turn to the problem of defining the scattering coordinate $\vec{\xi}$. From the way it occurs in (2.11), it is most usefully defined as the relative coordinate between the atomic centers of mass. This would make it nonsymmetric in the electrons as one can see from (2.3). The functions f_i can be used again to restore the symmetry of electrons in $\vec{\xi}$, but yield (2.3) when the bound state dissociates into the reference configuration. One such definition of a new coordinate system is

$$\vec{\rho} = M(\vec{\mathrm{R}}_1 + \vec{\mathrm{R}}_2) + m\textstyle\sum_i \vec{\mathrm{r}}_i / 2M_T \; , \qquad (2.13\mathrm{a})$$

$$\vec{\xi} = M(\vec{\mathrm{R}}_1 - \vec{\mathrm{R}}_2) + m\textstyle\sum_i f_i(\vec{\mathrm{r}}_i - \vec{\rho})/M_T \; , \qquad (2.13\mathrm{b})$$

$$\vec{\mathrm{x}}_i = \vec{\mathrm{r}}_i - \vec{\rho} \; . \qquad (2.13\mathrm{c})$$

The first of these is the usual total c.m., the last is the electronic coordinates measured from this c.m., and the second is the scattering coordinate in which the electrons enter symmetrically and which becomes (2.3) when multiplied by a function in the reference configuration. Note again that $\vec{\xi}$ is odd under interchange of the nuclei provided only that f_i is an odd function of $\vec{\xi}$.[6] Equation (2.13b) is an implicit relation for $\vec{\xi}$ because $\vec{\xi}$ enters in the f_i. An exact explicit relation is difficult to obtain but an explicit relation as a power series in (m/M) is easily gotten, and this is all we shall need.

The total Hamiltonian describing two He nuclei and four electrons must now be expressed in terms of the new coordinates. A straightforward transformation of the gradients yields (in the c.m. frame where $\nabla_\rho = 0$)[7]

$$\nabla_{\vec{R}_1} + \nabla_{R_2} = -(M/M_T)\textstyle\sum_i \nabla_i - (mM/M_T^2)\sum_i (\nabla_i f_i \vec{x}_i \cdot \nabla_\xi + f_i \nabla_\xi) + O(m/M)^2 \,,$$

$$\nabla_{R_1} - \nabla_{R_2} = (2M/M_T)\nabla_\xi + (2m/M_T)\textstyle\sum_i \nabla_\xi f_i \vec{x}_i \cdot \nabla_\xi + O(m/M)^2 \,,$$

$$\begin{aligned}\nabla_{r_i} = \nabla_{x_i} &+ (m/M_T)(f_i \nabla_\xi + \nabla_i f_i \vec{x}_i \cdot \nabla_\xi - \tfrac{1}{2}\textstyle\sum_j \nabla_j) + \tfrac{1}{2}(m/M_T)^2 \\ &\times [2 f_i \textstyle\sum_j \nabla_\xi f_j \vec{x}_j \cdot \nabla_\xi + 2\nabla_i f_i \vec{x}_i \cdot \sum_j \nabla_\xi f_j \vec{x}_j \cdot \nabla_\xi - \sum_j (\nabla_j f_j \vec{x}_j \cdot \nabla_\xi + f_j \nabla_\xi)] + O(m/M)^3.\end{aligned} \tag{2.14}$$

Before proceeding to the explicit construction of the total Hamiltonian in these variables, we pause to discuss the function $f_i = f(\vec{x}_i, \vec{\xi})$. The property (2.9) can be satisfied by[5]

$$f(\vec{x}, \vec{\xi}) = [(\vec{x} + \tfrac{1}{2}\vec{\xi})^2 - (\vec{x} - \tfrac{1}{2}\vec{\xi})^2]/[(\vec{x} + \tfrac{1}{2}\vec{\xi})^2 + (\vec{x} - \tfrac{1}{2}\vec{\xi})^2] = (\vec{x} \cdot \vec{\xi})/[x^2 + (\tfrac{1}{2}\xi)^2]. \tag{2.15}$$

Another type of function satisfying (2.9) is exemplified by

$$f(\vec{x}, \vec{\xi}) = \tanh[(\vec{x} \cdot \vec{\xi})/b^2] \,, \tag{2.16}$$

where b is an arbitrary real parameter. The presence of f in the coordinate transformation essentially represents a modification of the adiabatic states from the usual ones. The adiabatic (BO) representation is known to be violated by terms of relative order m/M or $m/M(Pa_0/\hbar)$, where P is the momentum associated with the relative atomic motion. For the energy range of interest here these are no larger than $(m/M)^{1/2}$. The choice of (2.15) for f would represent modifications of the adiabatic representation of order unity which would drastically change the physics of the description. We therefore discard this and turn to forms such as (2.16) where b^2 can be chosen large to make the modification of the adiabatic representation a small effect. If b^2 is chosen to be a number of order $(M/m)^{1/2} a_0^2$, where a_0 is the Bohr radius, then gradients of f will be small [order $(m/M)^{1/2}$] and the nonadiabatic terms thereby introduced will be no larger than the ones which occur in the usual calculations. Note, however, that if b^2 is chosen too large, equivalent long-range potentials are introduced. This can be seen by noting that the f_i appear in (2.13b) in order to give correct boundary conditions at infinite separations. The deviation from the correct boundary condition will act as a potential forcing the wave function to the correct form, so that in the large-ξ region, where f differs from ± 1, one will have an effective potential. Note that either form of f results in the relation $\vec{\xi}(R) = -\vec{\xi}(-R)$.

We now think of using (2.16) with

$$b^2 \sim a_0^2 (M/m)^{1/2}$$

so that to order m/M some of the gradient terms in (2.14) become negligible. The Hamiltonian then becomes

$$H = T + V \,, \tag{2.17a}$$

$$\begin{aligned}T = &- M_T^{-1}\nabla_\xi^2 + (m/2M_T^2)(4 - \textstyle\sum_i f_i^2)\nabla_\xi^2 + (4M_T)^{-1}(\sum_i \nabla_i)^2 - (2m)^{-1}\sum_i \nabla_i^2 \\ &- M_T^{-1}\textstyle\sum_i [f_i \nabla_i \cdot \nabla_\xi + \nabla_i f_i (\vec{x}_i \circ \nabla_\xi) \cdot \nabla_i + \nabla_i f_i \cdot \nabla_\xi + \tfrac{1}{2}\nabla_i^2 f_i \vec{x}_i \cdot \nabla_\xi] + (m/2M_T^2)(\sum_i f_i)(\sum_j \nabla_j) \cdot \nabla_\xi \,,\end{aligned} \tag{2.17b}$$

$$V = e^2\left[\frac{1}{|\vec{\xi} + 2\vec{\Lambda}|} + \sum_{i>j=1}^{4} (x_{ij})^{-1} - 2\sum_{i=1}^{4} \left(|\vec{x}_i - \tfrac{1}{2}\vec{\xi} - \vec{\Lambda} + \vec{\Delta}|^{-1} + |\vec{x}_i + \tfrac{1}{2}\vec{\xi} + \vec{\Lambda} + \vec{\Delta}|^{-1}\right)\right] \,, \tag{2.17c}$$

where
$$\vec{\Lambda} = (m/M)(\vec{\xi} - \tfrac{1}{2}\textstyle\sum_i f_i \vec{x}_i) \ ,$$
$$\vec{\Delta} = (m/2M)\textstyle\sum_i \vec{x}_i \ . \qquad (2.18)$$

Note that H is symmetric in all the electrons and in the reflection $\vec{\xi} \to -\vec{\xi}$.

Now we return to (2.11) and write

$$H = T_\xi + H_{\mathrm{ad}}(X, \vec{\xi}) \ , \qquad (2.19)$$

thereby defining T_ξ:

$$\begin{aligned} T_\xi = &-\frac{1}{M_T}\nabla_\xi{}^2 + \frac{m}{2M_T{}^2}(4 - \textstyle\sum_i f_i{}^2)\nabla_\xi{}^2 - \frac{1}{4M_T}\textstyle\sum_i \nabla_i{}^2 + \frac{1}{2M_T}\sum_{i>j}[\nabla_i \cdot \nabla_j - \tfrac{1}{2}(1 + f_i f_j)\nabla_i \cdot \nabla_j (1 + f_i f_j)] \\ &- \frac{1}{M_T}\textstyle\sum_i [f_i \nabla_i \cdot \nabla_\xi + \nabla_i f_i (\vec{x}_i \cdot \nabla_\xi) \cdot \nabla_i + \nabla_i f_i \cdot \nabla_\xi + \tfrac{1}{2}\nabla_i{}^2 f_i \vec{x}_i \cdot \nabla_\xi] + \frac{m}{2M_T{}^2}(\textstyle\sum_i f_i)(\sum_j \nabla_j) \cdot \nabla_\xi \\ &- 2e^2 \sum_{i=1}^{4} (|\vec{x}_i - \tfrac{1}{2}\vec{\xi} - \vec{\Lambda} + \vec{\Delta}|^{-1} - |\vec{x}_i - \tfrac{1}{2}\vec{\xi} + \vec{\Lambda}_i|^{-1} + |\vec{x}_i + \tfrac{1}{2}\vec{\xi} + \vec{\Lambda} + \vec{\Delta}|^{-1} - |\vec{x}_i + \tfrac{1}{2}\vec{\xi} + \vec{\Lambda}_i|^{-1}) \ , \end{aligned} \qquad (2.20)$$

where the $\vec{\Lambda}_i$ are given by (2.10).

The implication of (2.19) is that T_ξ is the perturbation of the adiabatic Hamiltonian due to the relative motion of the atoms. The terms proportional to e^2 in (2.20) have the appearance of a potential and have an interesting interpretation. They arise because in H_{ad} the positions of the c.m. of the individual atoms is fixed, not the positions of the nuclei. Thus, nuclear motion is included to some extent in H_{ad} so that the interaction between the electrons and nuclei is not exactly accounted for in H_{ad}. These terms are small, of order m/M times the usual potentials. The third and fourth terms in T_ξ contain no ∇_ξ operations and would appear to be better included in H_{ad}. Their inclusion would, however, destroy the property that the U_n dissociate into correct atomic wave functions. In addition, the scattering and coupling potentials will contain terms such as

$$-(M_T)^{-1} \int (dx) U_n{}^*(X, \vec{\xi}) \nabla_\xi{}^2 U_{n'}(X, \vec{\xi}) \ ,$$

the usual BO violating term which does not vanish for infinite $\vec{\xi}$. The third and fourth term are necessary to cancel it.

Now having written the total Hamiltonian in the form (2.19), we may formulate the scattering problem via the usual projection operator formalism.[8] We define a projection operator onto the ground state:

$$P = U_0\rangle\langle U_0 \ , \qquad (2.21)$$

and assume that no other channel is open and obtain an equation for the elastic scattering

$$P\Psi = F_0(\vec{\xi})U_0(X, \vec{\xi}) \ . \qquad (2.22)$$

The equivalent Hamiltonian entering the equation for $P\Psi$ is

$$H = P\{H + H[Q/(E - QHQ)]H\}P \ , \qquad (2.23)$$

where $Q = 1 - P$. The second term in (2.23) represents coupling to the closed channels. It will be treated below.

The first term yields an equivalent Hamiltonian for $F_0(\vec{\xi})$ of the form

$$\begin{aligned} h_\xi = &W_0(\xi) - M_T{}^{-1}\{\nabla_\xi{}^2 - (m/2M_T)\langle U_0(4 - \textstyle\sum_i f_i{}^2)U_0\rangle \nabla_\xi{}^2 + \langle U_0 \nabla_\xi{}^2 U_0\rangle + \tfrac{1}{4}\langle U_0 \sum_i \nabla_i{}^2 U_0\rangle - \tfrac{1}{2}\sum_{i>j} \\ &\times\langle U_0 | \nabla_i \cdot \nabla_j - \tfrac{1}{2}(1 + f_i f_j)\nabla_i \cdot \nabla_j (1 + f_i f_j) | U_0\rangle + \textstyle\sum_i \langle U_0 [f_i \nabla_i \cdot \nabla_\xi + \nabla_i f_i (\vec{x}_i \cdot \nabla_\xi) \cdot \nabla_i + \nabla_i f_i \cdot \nabla_\xi \end{aligned}$$

$$+\tfrac{1}{2}\nabla_i{}^2 f_i\vec{x}_i\circ\nabla_\xi]U_0\rangle-(m/2M_T)\langle U_0(4-\textstyle\sum_i f_i{}^2)\nabla_\xi{}^2U_0\rangle-(m/2M_T)\langle U_0\sum_i f_i\sum_j\nabla_j\cdot\nabla_\xi U_0\rangle\}$$

$$-\frac{1}{M_T}\textstyle\sum_i\langle U_0|f_i\nabla_i+\tfrac{1}{2}\nabla_i f_i|U_0\rangle\cdot\nabla_\xi-2e^2\sum_i\langle U_0||\vec{x}_i-\tfrac{1}{2}\vec{\xi}-\vec{\Lambda}+\vec{\Delta}|^{-1}-|\vec{x}_i-\tfrac{1}{2}\vec{\xi}+\vec{\Lambda}_i|^{-1}$$

$$+|\vec{x}_i+\tfrac{1}{2}\vec{\xi}+\vec{\Lambda}+\vec{\Delta}|^{-1}-|\vec{x}_i+\tfrac{1}{2}\vec{\xi}+\vec{\Lambda}_i|^{-1}|U_0\rangle\,. \qquad (2.24)$$

The first term is just the generalization of the usual adiabatic potential. The next two are the kinetic-energy operator with a position-dependent mass varying slightly from $M_T{}^2/M$ at $\xi=0$ to M_T at $\xi=\infty$. The Hamiltonian is nevertheless guaranteed to be Hermitian by the procedure through which it was obtained. The next four terms are the usual nonadiabatic correction plus the additional terms, of the same order introduced by a careful treatment of m/M effects. The two following terms are the same type but higher order in m/M. The next (∇_ξ) term is the usual velocity-dependent BO violating term generalized to our treatment here. Finally, the last term results from the offset between the center of mass of the atom and the nucleus. The power of m/M in it is less than that in the leading term by at least 1.

The eigenvalue W_0 appearing in (2.24) obtained from (2.12) can be expanded in powers of M^{-1}. If we retain only terms up to M^{-1} and substitute back into (2.24), still keeping only terms of that order, the result is

$$h_\xi=W_0{}^{(0)}(\xi)+(2M_T)^{-1}\langle U_0|\nabla_\xi{}^2+\tfrac{1}{2}\textstyle\sum_i\nabla_i{}^2+\sum_{i>j}\nabla_i\cdot\nabla_j+\sum_i[f_i\nabla_i\circ\nabla_\xi+\nabla_i f_i(\vec{x}_i\circ\nabla_\xi)\circ\nabla_i$$

$$+\nabla_i f_i\cdot\nabla_\xi+\tfrac{1}{2}\nabla_i{}^2 f_i\vec{x}_i\circ\nabla_\xi]|U_0\rangle-(M_T)^{-1}\langle U_0|\textstyle\sum_i(f_i\nabla_i+\tfrac{1}{2}\nabla_i f_i)U_0\rangle\circ\nabla_\xi-(M_T)^{-1}\nabla_\xi{}^2\;, \qquad (2.25)$$

where $W_0{}^{(0)}(\xi)$ is the usual eigenvalue obtained in the BO approximation. The terms containing f_i and those independent of ∇_ξ are not contained in the usual calculations of adiabatic scattering. The matrix elements coupling different channels, $\langle U_0|T_\xi|U_n\rangle$ will, of course, contain the new terms of (2.24) also. The new terms will be more important in this context than in (2.24) since the new terms are of order $(m/M)^{-1}$ compared to $W_0\sim 1$ in (2.24) whereas they will be the same order as the leading term in the coupling matrix since no $W(\xi)$ appears there. We now turn to the Q part of the equivalent Hamiltonian (2.23). We need to evaluate

$$\langle U_0|H[Q/(E-QHQ)]H|U_0\rangle\;, \qquad (2.26)$$

where Q projects off U_0. Then only that part of H enters (in the numerator) which will change the state U_0. These terms of T_ξ are of order $(M_T)^{-1}$ or smaller. Therefore, we may treat the denominator in lowest order in this parameter, in which case it is diagonal in the states. Then (2.26) may be written

$$\sum_{n\neq 0}\langle U_0|T_\xi|U_n\rangle(\xi)G_n(\vec{\xi},\vec{\xi}')\langle U_n|T_{\xi'}|U_0\rangle(\vec{\xi}')\;, \qquad (2.27)$$

where we have, to lowest order,

$$[E-W_n(\xi)+M^{-1}\nabla_\xi{}^2]G_n(\vec{\xi},\vec{\xi}')=\delta(\vec{\xi}-\vec{\xi}')\;. \qquad (2.28)$$

Note that $E=P^2/M_T+W_0(\infty)$ and that $W_n(\xi)-W_0(\infty)\gg P^2/M_T$ for our case. Then G_n is essentially independent of P^2, the incident energy, and so the potential is energy-independent. For the purposes of estimating (2.26), it is useful to think of $W_n(\xi)$ as a constant and replace

$$W_n-W_0=\beta_n{}^2$$

so that $G_n\simeq(M/4\pi)\,[\exp(-\beta_n M^{1/2}|\vec{\xi}-\vec{\xi}'|)/|\vec{\xi}-\vec{\xi}'|]\;.$

This shows that the potential is essentially local since the extent of the ξ' integral in the equation for F_0 is $M^{-1/2}$. The nonlocal potential (2.27) may then be replaced by a local one of the form

$$\sum_{n\neq 0}\langle U_0|T_\xi|U_n\rangle(\vec{\xi})\int d^3\xi' G_n(\vec{\xi},\vec{\xi}')\langle U_n|T_\xi|U_0\rangle(\vec{\xi})=-\sum_{n\neq 0}|\langle U_0|T_\xi|U_n\rangle|^2\;.$$

But the matrix element is proportional to M^{-1}, so that the total potential is proportional to M^{-2}. If we drop terms of this order, the effective Hamiltonian to this order is just (2.25).

The ∇_ξ term in (2.25) can be transformed away by a simple linear transformation which does not affect the boundary conditions, so that (2.25) can be thought of as a standard single-particle Schrödinger Hamiltonian with an energy-independent local potential. This is presumably the potential determined by the experiments on the second virial coefficient.

III. BOUND STATE

We now turn to the problem of the existence of bound states of two He atoms, i.e., of a stable He_2 molecule. The question is whether the phenomenological local-energy-independent potential determined from the second virial coefficient data can be used to make statements about this state. The virial coefficient essentially depends upon low-energy scattering phase shifts. The potential determined from this must then be extrapolated to negative energy to get bound state information. Can this be done?

It would be madness to use the Hamiltonian (2.19) based on the transformation (2.13) to try to calculate bound states. The transformation was designed to assure the correct scattering boundary conditions which are irrelevant to bound problems. However, for our purposes it is useful to continue to use the form (2.19) which is cumbersome but nevertheless still correct for bound states. We have seen that, to order $(m/M)^2$, an essentially energy-independent local potential can be defined for the one-channel scattering problem. A similar one-channel problem (2.21)–(2.23) can be defined for the bound state. The energy dependence again comes in through the Q part of space and again, since the binding energy of He_2 will be very small (if it exists at all), this energy dependence will be negligible. Therefore, the same potential will occur in the bound-state problem as occurred in the scattering problem, so that the phenomenologically determined potential will be the correct one to use for investigating whether a bound state exists.

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[6] This will make it easy to preserve the g or u symmetry of the total wave function.

[7] Here and below a derivative operator is meant to operate only on the function immediately to its right, and the dot signifies an inner product between the two vectors immediately flanking it.

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