Nonadiabatic formulation of the slow-atomic-collision problem in the finite electronic basis

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The resonating-group method developed for nuclear collisions is used to obtain equations describing the collisions of slow atoms. On one hand, these equations correctly take into account the indistinguishability of electrons and scattering boundary conditions and therefore are free from the drawbacks of conventional equations in the adiabatic electronic basis. On the other hand, they retain the form of the latter equations and therefore are in agreement with the generally accepted picture of heavy-particle motion in the fields of adiabatic electronic potentials accompanied by nonadiabatic transitions. The general theory is illustrated by considering the interaction of two ground-state hydrogen atoms in the Heitler-London electronic basis.

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I. INTRODUCTION

Recently collisions of cold atoms (with kinetic energies from $\sim 10^{-3}$ to $\sim 10^{2}$ K) attracted great interest of investigators in the field of atomic physics in connection with such problems as laser trapping of atoms [1–5], hydrogen maser operation [6–9], and behavior of the spin-polarized atoms [10–12].

It seems at first sight that at least for two H atoms the problem of the theoretical treatment of slow collision is purely numerical since the lowest singlet and triplet accurate potential-energy curves are known for this system [13–15]. But a more detailed study performed in [6] showed that this is not so.

The hyperfine-induced spin-exchange collision frequency shift of hydrogen maser oscillations at temperatures 0.05–50 K were calculated in [6]. The s-wave contribution to the hyperfine-induced frequency shift cross section showed a remarkable sensitivity to the reduced mass μ adopted for the description of the H-H collision. Replacing $\mu=\frac{1}{2}M$ (M being the proton mass) by the very close value $\frac{1}{2}M_{\mathrm{H}}$ where $M_{\mathrm{H}}=M+m_e$ is the atomic mass (m_e being the electron mass) leads to changes up to 50% in this contribution.

In the case of singlet scattering, a deep potential well is present. The relative motion of the H atoms within this well is quasiclassical even at zero relative kinetic energy ε_t and because of this there is nothing astonishing in the above-noted large reduced-mass effect. Actually, on the one hand for $\varepsilon_t < 10$ K, only the s scattering is important and the cross section is determined by the scattering length $a=\lim_{k\to 0}[-(\tan\delta_0)/k]$ [16] where k is a relative motion wave number and δ_0 is an s-scattering phase shift. On the other hand, because of the quasiclassical nature of the relative motion within the well the radial wave function oscillates rapidly and $\delta_0 \gg 1$ for $k\to 0$. Therefore the scattering length is extremely sensitive to the variation of the parameters of the radial Schrödinger equation including the reduced mass. This fact can be easily illustrated in the example of the square potential well.

It is to be noted that such a strong dependence on the reduced mass may also take place for the very low energies in the case of inelastic collisions, which can be described by the Landau-Zener-Stuekelberg model (see, e.g., [17]). At such energies only one (or a few) partial wave contributes to the cross section and if regions of quasiclassical radial motion exist, the cross section will be directly proportional to the $\cos^2\Phi_{\mathrm{St}}$, where the Stueckelberg phase $\Phi_{\mathrm{St}} \gg 1$. Again the cross section appears to be very sensitive to small variations of the parameters of the problem, including the reduced mass.

Generally it can be said that experiments involving collisions of cold atoms belong to the class of high-resolution experiments with intrinsically quasiclassical systems. And it was argued many times (see, e.g., [18,19]) that for such experiments the semiclassical picture of molecular motion, based upon the Born-Oppenheimer approximation, may become inadequate.

The sensitivity of the cross sections to the difference between nuclear and atomic masses noted above is a strong indication of such a situation. In practice, at least at large internuclear distances, since the atoms are colliding but not the nuclei, the choice of $\mu=\frac{1}{2}M_{\mathrm{H}}$ is made. In [6] $\mu=\frac{1}{2}M_{\mathrm{H}}$ was taken for all internuclear distances. It is to be noted here that in [20], trying to reproduce experimental highly excited vibrational levels of H_2 on the basis of the best Kolos-Wolniewicz potential for the $X\,^1\Sigma_g^+$ state, the authors had to fit an effective value for the reduced mass and obtained a value very near to $\frac{1}{2}M_{\mathrm{H}}$.

But such a choice is incompatible with the Born-Oppenheimer picture where the nuclei are assumed to move in the fields of adiabatic electronic potentials—eigenenergies of the electronic Hamiltonian for clamped nuclei to which the so-called adiabatic correction is added (see, e.g., [13]). The reduced mass of the nuclei enters the set of coupled equations corresponding to this picture

in the molecular (adiabatic, perturbed-stationary states) basis, governing the motion of heavy particles (see, e.g., [17]).

It is obvious that this difficulty with the reduced mass of heavy particles is similar to the difficulties facing collision theorists due to the use of the molecular basis for treating an atomic-collision problem (see, e.g., [17]). The aim of the present work is to show that they can be removed in the finite electronic basis using the resonating-group method (RGM) suggested in the works of Wheeler [21] as early as in 1937. On the one hand the resulting equations assume the familiar form they have in the usual molecular basis formulation, but on the other hand they are free from the difficulties met in the conventional use of this basis. To make the derivation more clear we present here the simplest formulation of the method for the collision of two nonrelativistic H atoms with distinguishable structureless nuclei. Additionally, it is assumed that the finite electronic basis includes only spherically symmetric atomic s states. Collisions of one-electron atoms with nonzero electronic angular momenta and non-Coulomb cores with different masses as well as of two many-electron atoms can also readily be treated by the method presented here. Such a generalization will be considered in a forthcoming paper.

The paper is organized as follows. In Sec. II the position of the problem and the general ideas of the present approach are briefly discussed. In Sec. III the general form of the RGM equations for the scattering of two H atoms is given. Section IV is devoted to the derivation of the differential RGM scattering equations based on the narrow kernel approximation. In Sec. V the molecular-basis-coupled radial Schrödinger equations are derived from the differential RGM equations. In Sec. VI the general approach is illustrated considering the interaction between two ground-state hydrogen atoms within the basis including only ground-state hydrogen wave functions. This approximation can be called the "nonadiabatic Heitler-London approximation" (NAHLA). Sections VII and VIII are devoted to the discussion and conclusions. Calculations of some integrals arising in NAHLA are considered in the Appendix. Atomic units with $\hbar = m_e = e = 1$ are used throughout the text unless stated otherwise.

II. POSITION OF THE PROBLEM

A. Difficulties of the conventional approach

The conventional formulation of the atomic collision problem in the adiabatic basis suffers from the following difficulties:

(1) spurious behavior of the nonadiabatic coupling matrix elements at large internuclear distances R_{12}—some of them decrease as slowly as $1/R_{12}$ and some tend even to constant values as $R_{12} \to \infty$; and

(2) dependence of the nonadiabatic coupling on the choice of the common origin for the electronic coordinates.

These difficulties were intensively studied and a large number of papers on this subject appeared in the literature. A comprehensive discussion of the results obtained can be found in the reviews [22–25], see also [17]. Most important for the present development is a clear understanding of the fact that the above difficulties are not due to the adiabatic approximation as such (see, e.g., [17,26]). The root of the difficulties is the indistinguishability of electrons due to which collision of two atoms is, in fact, always a rearrangement collision. Therefore it is impossible to introduce in a simple way a unique coordinate characterizing the distances between the atomic centers of mass in different arrangement channels. From this principle point of view the situations in the cases of collisions of neutrals and charge transfer, where there are two arrangement channels corresponding to the binding of an electron to two different cores, are analogous. As a result, adiabatic basis wave functions do not obey correct scattering boundary conditions. It is emphasized in many papers (see, e.g., [27,28]) that these conditions can be fulfilled in the adiabatic basis only if the complete set of adiabatic states including the continuum is taken into account.

The majority of concrete methods for treating the difficulties connected with the use of the adiabatic basis concern the charge-transfer problem, which is reduced to the three-body problem: two heavy cores and one light electron. Therefore almost all of them cannot be applied to take into account the indistinguishability problem in the case of collisions of neutrals where at least two mutually exchanging electrons are to be considered. To our knowledge for the latter case the only well-developed theory is due to Mittleman and Tai [29] (see also [17]) in which the two above-mentioned problems with the nonadiabatic couplings are removed. But, alongside the usual adiabatic basis, it includes not uniquely defined switching functions. To exclude the dependence of the results on the choice of the switching functions, the calculations are to be performed accounting for the complete adiabatic basis set.

As for the reduced-mass problem, only attempts of a semiempirical nature that introduce an effective reduced mass especially suited for the bound-state calculations can be mentioned [20,30,31].

Thus, in light of the above-emphasized principally high sensitivity of the cold-atom collision characteristics to the parameters entering scattering equations, the following dilemma arises. On the one hand, it is, of course, desirable to use that large amount of information on adiabatic electronic potentials that quantum chemistry provides and an appealing concept of heavy-particle motion in the fields of these potentials accompanied by nonadiabatic transitions. On the other hand, the available coupled scattering equations corresponding to this picture contain principal drawbacks.

It seems to us that this dilemma originates from the asymmetry of the commonly used molecular basis approach to the atomic collision problem. Scattering equations as mentioned above are such that contradictions do not arise only if the complete set of the adiabatic electronic states is taken into account. But, quantum-chemical calculations of adiabatic electronic terms and wave functions which enter these equations are always

performed in some finite basis of the square integrable electronic functions.

B. Present approach to the problem

To overcome this asymmetry and get an equal state of adiabatic and nonadiabatic parts of the atomic collision problem, it seems natural to invert the standard formulation. As a first step, take some finite electronic basis, forget about the small electronic mass and, accurately taking into account the indistinguishability of electrons, derive a set of coupled scattering equations that correspond to this basis and that is compatible with the correct boundary conditions. As a second step, try to see whether it is possible, using the small value of the ratio m_e/M_n (M_n is a characteristic nuclear mass), to obtain simplified equations which possess the desirable properties. Namely, these simplified equations must be compatible with the correct scattering boundary conditions and correspond to the familiar intuitive picture of the heavy-particle motion in the fields of adiabatic potentials accompanied by nonadiabatic transitions.

In fact, as for the first step, a formulation exists. It was developed to treat collisions of complex nuclei where the problem of simultaneous accounting for the correct scattering boundary conditions and the indistinguishability of nucleons belonging to different nuclei also exist, but in this case masses of all the particles are of the same order. This is called the resonating-group method (RGM) suggested by Wheeler [21]. Since then, the RGM was successfully applied to a variety of concrete nuclear collisions and its mathematical structure was thoroughly investigated. A comprehensive account of all the subjects concerning RGM can be found in Refs. [32–37]. Independently similar equations for the charge-transfer process in the ion-atom collision were written by Mott and Massey [16].

The starting idea for the second step, based on the use of the expansion over moments of the originally nonlocal (RGM) equations, was suggested in [38,39] in connection with the nuclear structure calculations. A similar idea was used by Delos [22,23] in his consideration of the charge transfer based on the equations from [16].

III. RESONATING-GROUP METHOD EQUATIONS

A. Hamiltonian

The diatom H-H, which consists of two electrons e_1 and e_2 and two protons p_1 and p_2 mutually interacting by the Coulomb forces, is described in the center-of-mass space fixed-coordinate frame. See Fig. 1 for notations. Since electron exchange must be taken into account, two equivalent sets of the relative Jacobi coordinates are to be used.

The first set, $\mathbf{r}_1^{(1)}$, $\mathbf{r}_2^{(1)}$, and $\mathbf{R}^{(1)}$ (see Table I), corresponds to the situation where e_1 is bound to p_1 and e_2 to p_2 and will be called the reference arrangement (RA). The second set, $\mathbf{r}_1^{(2)}$, $\mathbf{r}_2^{(2)}$, and $\mathbf{R}^{(2)}$, corresponds to the situation where e_1 is bound to p_2 and e_2 to p_1 and it will be called the transposed arrangement (TA).

The Hamiltonian of the H_2-system in the RA has the form

$$H = T_{\text{rel}}^{(1)} + H_1^{(1)} + H_2^{(1)} + V^{(1)} , \tag{3.1}$$

where $T_{\text{rel}}^{(1)}$ is the relative kinetic energy,

TABLE I. Vectors characterizing relative positions of particles in the H_2 system.

	Jacobi coordinates	
	Reference arrangement (RA)	Transposed arrangement (TA)
Radii vectors between electrons and protons	$\mathbf{r}_1^{(1)}=\mathbf{r}_1^e-\mathbf{R}_1^p$ $\mathbf{r}_2^{(1)}=\mathbf{r}_2^e-\mathbf{R}_2^p$	$\mathbf{r}_1^{(2)}=\mathbf{r}_2^e-\mathbf{R}_1^p$ $\mathbf{r}_2^{(2)}=\mathbf{r}_1^e-\mathbf{R}_2^p$
Radii vectors between atomic centers of mass	$\mathbf{R}^{(1)}=\frac{1}{M+1}(M\mathbf{R}_2^p+\mathbf{r}_2^e)-\frac{1}{M+1}(M\mathbf{R}_1^p+\mathbf{r}_1^e)$	$\mathbf{R}^{(2)}=\frac{1}{M+1}(M\mathbf{R}_2^p+\mathbf{r}_1^e)-\frac{1}{M+1}(M\mathbf{R}_1^p+\mathbf{r}_2^e)$
Interrelations	$\mathbf{r}_1^{(1)}=\frac{1}{M+1}(\mathbf{r}_1^{(2)}+M\mathbf{r}_2^{(2)})+\mathbf{R}^{(2)}$ $\mathbf{r}_2^{(1)}=\frac{1}{M+1}(M\mathbf{r}_1^{(2)}+\mathbf{r}_2^{(2)})-\mathbf{R}^{(2)}$ $\mathbf{R}^{(1)}=\frac{2M}{(M+1)^2}(\mathbf{r}_1^{(2)}-\mathbf{r}_2^{(2)})+\frac{M-1}{M+1}\mathbf{R}^{(2)}$	$\mathbf{r}_1^{(2)}=\frac{1}{M+1}(\mathbf{r}_1^{(1)}+M\mathbf{r}_2^{(1)})+\mathbf{R}^{(1)}$ $\mathbf{r}_2^{(2)}=\frac{1}{M+1}(M\mathbf{r}_1^{(1)}+\mathbf{r}_2^{(1)})-\mathbf{R}^{(1)}$ $\mathbf{R}^{(2)}=\frac{2M}{(M+1)^2}(\mathbf{r}_1^{(1)}-\mathbf{r}_2^{(1)})+\frac{M-1}{M+1}\mathbf{R}^{(1)}$

Radius vector between electrons $\mathbf{r}_{12}$

$$\mathbf{r}_{12}=\frac{M}{M+1}(\mathbf{r}_2^{(1)}-\mathbf{r}_1^{(1)})+\mathbf{R}^{(1)}=\mathbf{r}_2^e-\mathbf{r}_1^e$$

Radius vector between protons $\mathbf{R}_{12}$

$$\mathbf{R}_{12}=\mathbf{R}^{(1)}+\frac{1}{M+1}(\mathbf{r}_1^{(1)}-\mathbf{r}_2^{(1)})=\mathbf{R}_2^p-\mathbf{R}_1^p$$

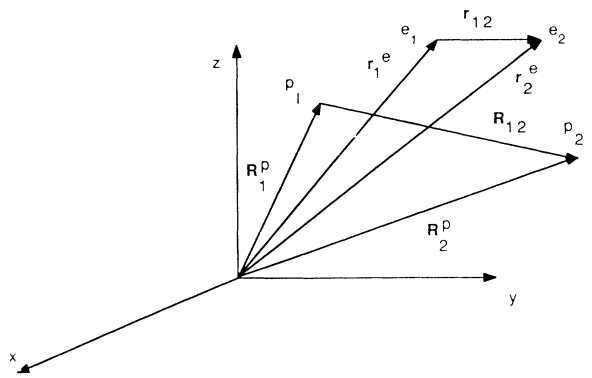

FIG. 1. Coordinates of electrons e_1 and e_2 and protons p_1 and p_2 in the space fixed frame (x,y,z).

$$T_{\text{rel}}^{(1)} = -\frac{1}{M+1}\nabla^2_{\mathbf{R}^{(1)}} , \tag{3.2}$$

$H_1^{(1)}$ and $H_2^{(1)}$ are the electronic Hamiltonians,

$$H_i^{(1)} = -\frac{M+1}{2M}\nabla^2_{\mathbf{r}_i^{(1)}} - \frac{1}{r_i^{(1)}}, \quad i=1,2 \tag{3.3}$$

and $V^{(1)}$ is an interaction in RA.

$$V^{(1)} = \frac{1}{R_{12}} + \frac{1}{r_{12}} - \frac{1}{r_1^{(2)}} - \frac{1}{r_2^{(2)}} , \tag{3.4}$$

where R_{12}, r_{12}, $r_1^{(2)}$, and $r_2^{(2)}$ are expressed as functions of $\mathbf{r}_1^{(1)}$, $\mathbf{r}_2^{(1)}$, and $\mathbf{R}^{(1)}$ (see Table I). Relations similar to Eqs. (3.1)–(3.4) can be written in the TA by substituting the upper indices (1) by (2).

B. Wave functions

Our aim is to construct a two-electron—two-nuclei wave function which will be antisymmetric with respect to permutations of electrons and compatible with the correct scattering boundary conditions. The spin functions are factorized and only spatial parts of the singlet and triplet wave functions may be considered independently. Explicit consideration will be performed for the singlet states with the even under electron permutation spatial wave functions. The corresponding formulas for the triplet case can be deduced from those for the singlet one by an obvious change of signs.

RGM accepts the following form for the electron-nuclear wave function Ψ with the desired properties:

$$\Psi = \sum_{n_1}\sum_{n_2}\frac{1}{\sqrt{2}}\{\varphi^f_{n_1}(\mathbf{r}_1^{(1)})\varphi^f_{n_2}(\mathbf{r}_2^{(1)})g_{n_1n_2}(\mathbf{R}^{(1)}) + \varphi^f_{n_1}(\mathbf{r}_1^{(2)})\varphi_{n_2}(\mathbf{r}_2^{(2)})g_{n_1n_2}(\mathbf{R}^{(2)})\} , \tag{3.5}$$

where the sum runs over a finite number of electronic atomic states with the angular momentum $l=0$ for the simplified case treated here. The corresponding atomic orbitals are eigenfunctions of the atomic Hamiltonians $H_i^{(j)}$ [Eq. (3.3)]

$$H_i^{(j)}\varphi^f_{n_i}(\mathbf{r}_i^{(j)}) = \varepsilon^f_{n_i}\varphi^f_{n_i}(\mathbf{r}_i^{(j)}) \tag{3.6}$$

with eigenenergies $\varepsilon^f_{n_i}$, where $i=1,2$, $j=1,2$, and n_i are principal quantum numbers. The functions $g_{n_1n_2}(\mathbf{R}^{(j)})$ play the role of variational amplitudes.

The functions $\varphi^f_{n_i}(\mathbf{r}_i^{(j)})$ and energies $\varepsilon^f_{n_i}$ take into account finite values of proton masses. In practical quantum-chemical calculations, the functions $\varphi_{n_i}(\mathbf{r})$ and energies ε_{n_i} corresponding to infinitely heavy nuclei are used. For the H atom they are related to $\varphi^f_{n_i}(\mathbf{r})$ and $\varepsilon^f_{n_i}$ in the following simple way:

$$\varphi^f_{n_i}(\mathbf{r}) = \left[\frac{M}{M+1}\right]^{3/2}\varphi_{n_i}\left[\frac{M}{M+1}\mathbf{r}\right] , \tag{3.7}$$

$$\varepsilon^f_{n_i} = \varepsilon_{n_i}\frac{M}{M+1} , \tag{3.8}$$

where M is the proton mass.

The wave function (3.5) is different from the corresponding trial electron-nuclear wave functions of the conventional atomic collision theory (see, e.g., [17]). In the former, symmetrization with respect to electron permutation affects both basis electronic atomic functions and amplitudes $g_{n_1n_2}$ describing the relative motion of atoms. In the latter, only basis electronic functions will be symmetrized.

By introducing the δ function, Ψ can be given a more suitable form for physical interpretation and for further consideration (see, e.g., [34]):

$$\Psi = \sum_{n_1}\sum_{n_2}\int d^3\mathbf{R}\, g_{n_1n_2}(\mathbf{R})|\mathbf{R}n_1n_2\rangle . \tag{3.9}$$

Here, $\mathbf{R}$ is the so-called parameter coordinate characterizing the distance between the atomic centers of mass regardless of the distribution of electrons between the atoms, and

$$|\mathbf{R}n_1n_2\rangle = \frac{1}{\sqrt{2}}\{\delta(\mathbf{R}-\mathbf{R}^{(1)})\varphi^f_{n_1}(\mathbf{r}_1^{(1)})\varphi^f_{n_2}(\mathbf{r}_2^{(1)}) + \delta(\mathbf{R}-\mathbf{R}^{(2)})\varphi^f_{n_1}(\mathbf{r}_1^{(2)})\varphi^f_{n_2}(\mathbf{r}_2^{(2)})\} \tag{3.10}$$

is the nonorthogonal basis electron-nuclear function, corresponding to two atoms at a distance $\mathbf{R}$. The amplitudes $g_{n_1n_2}(\mathbf{R})$ may be interpreted as wave functions of the relative atomic motion though in the limited sense because of the nonorthogonality of the basis $|\mathbf{R}n_1n_2\rangle$.

C. RGM equations and their general properties

The application of the variational principle to Ψ in the form (3.9), considering $g_{n_1n_2}(\mathbf{R})$ as variational amplitudes, leads to RGM equations for $g_{n_1n_2}(\mathbf{R})$ [21,32–37]:

$$\sum_{n_1'}\sum_{n_2'}\int d^3\mathbf{R}'\langle n_1n_2\mathbf{R}|H-E|\mathbf{R}'n_1'n_2'\rangle g_{n_1'n_2'}(\mathbf{R}') = 0 , \tag{3.11}$$

where E is the total energy of the H_2 system, corresponding to the Hamiltonian H given by Eqs. (3.1)–(3.4). Using the RA variables, one obtains for the matrix element in Eq. (3.11):

$$\langle n_1 n_2 \mathbf{R}|H-E|\mathbf{R}' n_1' n_2'\rangle = \frac{1}{2}\int d^3\mathbf{R}^{(1)} d^3\mathbf{r}_1^{(1)} d^3\mathbf{r}_2^{(1)} \times[\varphi_{n_1}^f(\mathbf{r}_1^{(1)})\varphi_{n_2}^f(\mathbf{r}_2^{(1)})\delta(\mathbf{R}^{(1)}-\mathbf{R})+\varphi_{n_1}^f(\mathbf{r}_1^{(2)})\varphi_{n_2}^f(\mathbf{r}_2^{(2)})\delta(\mathbf{R}^{(2)}-\mathbf{R})](H-E) \times[\varphi_{n_1'}^f(\mathbf{r}_1^{(1)})\varphi_{n_2'}^f(\mathbf{r}_2^{(1)})\delta(\mathbf{R}^{(1)}-\mathbf{R}')+\varphi_{n_2'}^f(\mathbf{r}_1^{(2)})\varphi_{n_1'}^f(\mathbf{r}_2^{(2)})\delta(\mathbf{R}^{(2)}-\mathbf{R}')] . \quad (3.12)$$

Here Eq. (3.1) is to be used for H and $\mathbf{r}_1^{(2)}$, $\mathbf{r}_2^{(2)}$, and $\mathbf{R}^{(2)}$ are to be considered as functions of $\mathbf{r}_1^{(1)}$, $\mathbf{r}_2^{(1)}$, and $\mathbf{R}^{(1)}$ (see Table I). Note that the s functions φ_n^f are real and therefore all the matrix elements in this paper are also real.

Using the invariance of H under the transformation $\mathbf{r}_1^{(1)}$, $\mathbf{r}_2^{(1)}$, $\mathbf{R}^{(1)}\rightarrow\mathbf{r}_1^{(2)},\mathbf{r}_2^{(2)},\mathbf{R}^{(2)}$ and the fact that φ_n^f are eigenfunctions of the atomic Hamiltonian $H_i^{(j)}$ [see Eq. (3.3)] with eigenenergies $\varepsilon_{n_i}^f$ then Eq. (3.11) can be given a more familiar form:

$$\sum_{n_1'}\sum_{n_2'}\left\{\left[-\frac{1}{M+1}\nabla^2+\varepsilon_{n_1}^f+\varepsilon_{n_2}^f-E\right]\delta_{n_1 n_1'}\delta_{n_2 n_2'}+\langle n_1 n_2|Q(\mathbf{R})|n_1' n_2'\rangle\right\}g_{n_1' n_2'}(\mathbf{R}) +\sum_{n_1'}\sum_{n_2'}\int d^3\mathbf{R}'\langle n_1 n_2 \mathbf{R}|K|\mathbf{R}' n_1' n_2'\rangle g_{n_1' n_2'}(\mathbf{R}')=0 , \quad (3.13)$$

where,

$$\langle n_1 n_2|Q(\mathbf{R})|n_1' n_2'\rangle = \int d^3\mathbf{r}_1^{(1)} d^3\mathbf{r}_2^{(1)}\varphi_{n_1}^f(\mathbf{r}_1^{(1)})\varphi_{n_2}^f(\mathbf{r}_2^{(1)})V^{(1)}(\mathbf{R})\varphi_{n_1'}(\mathbf{r}_1^{(1)})\varphi_{n_2'}(\mathbf{r}_2^{(1)}) \quad (3.14)$$

is a matrix of Coulomb integrals [$V^{(1)}(\mathbf{R})$ is given by Eq. (3.4) with $\mathbf{R}$ substituted for $\mathbf{R}^{(1)}$]. It differs from the conventional matrix of Coulomb integrals in quantum chemistry because here, $V^{(1)}$ and the electronic wave functions take into account the difference between the centers of masses of atoms and the positions of the corresponding nuclei.

The nonlocal kernel $\langle n_1 n_2 \mathbf{R}|K|\mathbf{R}' n_1' n_2'\rangle$ describes electron exchange and its explicit expression is as follows:

$$\langle n_1 n_2 \mathbf{R}|K|\mathbf{R}' n_1' n_2'\rangle = \frac{1}{2}\int d^3\mathbf{R}^{(1)} d^3\mathbf{r}_1^{(1)} d^3\mathbf{r}_2^{(1)}\{[\varphi_{n_1}^f(\mathbf{r}_1^{(1)})\varphi_{n_2}^f(\mathbf{r}_2^{(1)})\delta(\mathbf{R}-\mathbf{R}^{(1)})(H-E)\varphi_{n_1'}^f(\mathbf{r}_1^{(2)})\varphi_{n_2'}^f(\mathbf{r}_2^{(2)})\delta(\mathbf{R}'-\mathbf{R}^{(2)})] +[\varphi_{n_1}^f(\mathbf{r}_1^{(2)})\varphi_{n_2}^f(\mathbf{r}_2^{(2)})\delta(\mathbf{R}-\mathbf{R}^{(2)})(H-E)\varphi_{n_1'}^f(\mathbf{r}_1^{(1)})\varphi_{n_2'}^f(\mathbf{r}_2^{(1)})\delta(\mathbf{R}'-\mathbf{R}^{(1)})]\} . \quad (3.15)$$

Due to the hermiticity of H and $V^{(1)}$ the matrix of the Coulomb integrals and the nonlocal exchange kernel are hermitian. Then

$$\langle n_1 n_2|Q(\mathbf{R})|n_1' n_2'\rangle = \langle n_1' n_2'|Q(\mathbf{R})|n_1 n_2\rangle \quad (3.16)$$

and

$$\langle n_1 n_2 \mathbf{R}|K|\mathbf{R}' n_1' n_2'\rangle = \langle n_1' n_2' \mathbf{R}'|K|n_1 n_2 \mathbf{R}\rangle . \quad (3.17)$$

It is to be noted in connection with Eq. (3.15) that because the electron permutation operator commutes with H, the two terms in square brackets on the right-hand side (rhs) of Eq. (3.15) give equal contributions to the kernel. This fact is not used here as is usually done [33–36] to simplify the kernel because of the following reasons. We are going to simplify Eq. (3.13) using the smallness of $1/M$. The total Hamiltonian includes the operators $T_{\text{rel}}^{(1)}$ and $V^{(1)}$ (or $T_{\text{rel}}^{(2)}$ and $V^{(2)}$) which are principally different from the point of view of such simplifications. Therefore their contributions are to be considered separately and it is desirable that the corresponding kernels possess an important property of hermiticity. But since separately $T_{\text{rel}}^{(1)}$ and $V^{(1)}$ (or $T_{\text{rel}}^{(2)}$ and $V^{(2)}$) do not commute with the electron permutation operator, commutation can be achieved only by using the symmetrical expression (3.15).

In order to obtain suitable final expressions for the matrix of Coulomb integrals and the exchange kernel, the following transformations are to be made:

$$\mathbf{r}_1^{(1)}=\frac{M+1}{M}\mathbf{r}_1;\quad \mathbf{r}_2^{(1)}=\frac{M+1}{M}\mathbf{r}_2 . \quad (3.18)$$

It allows us to eliminate the mass dependent scaling factor from the atomic wave functions [see Eq. (3.7)] and to get all the expressions in terms of the generally accepted wave functions φ_{n_i} for infinitely heavy nuclei.

After these transformations one obtains for the Coulomb matrix elements

$$\langle n_1 n_2|Q(\mathbf{R})|n_1' n_2'\rangle = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2\varphi_{n_1}(\mathbf{r}_1)\varphi_{n_2}(\mathbf{r}_2)V(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})\varphi_{n_1'}(\mathbf{r}_1)\varphi_{n_2'}(\mathbf{r}_2) \quad (3.19)$$

with

$$V(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})=\left|\mathbf{R}+\frac{1}{M}(\mathbf{r}_1-\mathbf{r}_2)\right|^{-1}+|\mathbf{r}_1-\mathbf{r}_2-\mathbf{R}|^{-1}-\left|\mathbf{r}_1-\mathbf{R}+\frac{1}{M}\mathbf{r}_2\right|^{-1}-\left|\mathbf{r}_2+\mathbf{R}+\frac{1}{M}\mathbf{r}_1\right|^{-1} . \quad (3.20)$$

As for the exchange kernel, after transformation (3.18) and integration over $d^3\mathbf{R}^{(1)}$ with the help of $\delta(\mathbf{R}^{(1)}-\mathbf{R}')$ the final expression with the separated contributions of $T_{\text{rel}}^{(j)}$ and $V^{(j)}$ is as follows:

$$\langle n_1 n_2 \mathbf{R}|K|\mathbf{R}' n_1' n_2'\rangle = [\tfrac{1}{2}(\varepsilon_{n_1}^f+\varepsilon_{n_2}^f+\varepsilon_{n_1'}^f+\varepsilon_{n_2'}^f)-E]\langle n_1 n_2 \mathbf{R}|S|\mathbf{R}' n_1' n_2'\rangle + \langle n_1 n_2 \mathbf{R}|T|\mathbf{R}' n_1' n_2'\rangle + \langle n_1 n_2 \mathbf{R}|V|\mathbf{R}' n_1' n_2'\rangle \ , \tag{3.21}$$

where (suppressing here and everywhere below the indices $n_1 n_2$; $n_1' n_2'$ in the notations of the matrix elements)

$$\langle \mathbf{R}|S|\mathbf{R}'\rangle = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 F(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})\delta\left(\mathbf{R}'-\mathbf{R}-\frac{2}{M+1}\rho\right) \tag{3.22}$$

is an overlap kernel.

$$\langle \mathbf{R}|T|\mathbf{R}'\rangle = -\frac{1}{2(M+1)}(\nabla_{\mathbf{R}}^2+\nabla_{\mathbf{R}'}^2)\langle \mathbf{R}|S|\mathbf{R}'\rangle \tag{3.23}$$

is a relative kinetic energy kernel, and

$$\langle \mathbf{R}|V|\mathbf{R}'\rangle = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 V_{\text{sym}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})F(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})\delta\left(\mathbf{R}'-\mathbf{R}-\frac{2}{M+1}\rho\right) \tag{3.24}$$

is an interaction kernel.

The expressions for $F(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})$, ρ and $V_{\text{sym}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})$ are as follows:

$$F(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R}) = \varphi_{n_1}(\mathbf{r}_1)\varphi_{n_2}(\mathbf{r}_2)\varphi_{n_1'}\left(\mathbf{r}_2+\mathbf{R}+\frac{1}{M+1}\rho\right)\varphi_{n_2'}\left(\mathbf{r}_1-\mathbf{R}-\frac{1}{M+1}\rho\right) , \tag{3.25}$$

$$\rho = \mathbf{r}_1-\mathbf{r}_2-\mathbf{R} \ , \tag{3.26}$$

$$V_{\text{sym}}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R}) = \left|\mathbf{R}+\frac{1}{M}(\mathbf{r}_1-\mathbf{r}_2)\right|^{-1}+|\mathbf{r}_1-\mathbf{r}_2-\mathbf{R}|^{-1} - \frac{1}{2}\left\{\frac{M}{M+1}r_1^{-1}+\frac{M}{M+1}r_2^{-1}+\left|\mathbf{r}_1-\mathbf{R}+\frac{1}{M}\mathbf{r}_2\right|^{-1}+\left|\mathbf{r}_2+\mathbf{R}+\frac{1}{M}\mathbf{r}_1\right|^{-1}\right\} . \tag{3.27}$$

It can be readily verified that all three kernels entering the total exchange kernel are separately hermitian.

IV. DIFFERENTIAL RGM EQUATIONS IN THE NARROW KERNEL APPROXIMATION

A. Narrow kernel approximation and general consideration

The RGM equations introduced in Sec. III solve the problem of simultaneously accounting for the correct boundary conditions and indistinguishability of electrons using a unique coordinate describing the relative motion of atoms. However, the price of it is very high because these equations are nonlocal. There is no doubt that the conventional picture of an atomic collision based on the local equations in the molecular basis is correct in its main features. Therefore it is natural to expect that due to the small value of $1/M$, entering the RGM equations integral operator differs little from a differential one.

The nonlocality of the RGM equations is a consequence of the fluctuations of the radius vector between the atomic centers of mass about the radius vector $\mathbf{R}_{12}$ between nuclei. Because $1/M$ is small and because in the bound atomic states electrons cannot go far away from the nuclei following the fluctuations

$$\delta\mathbf{R}^{(1),(2)} = \mathbf{R}^{(2)}-\mathbf{R}^{(1)} = \frac{2}{M+1}(\mathbf{r}_1-\mathbf{r}_2-\mathbf{R}^{(1)}) \tag{4.1}$$

are small in comparison with $\mathbf{R}^{(1)}$, $\mathbf{R}^{(2)}$, and $\mathbf{R}_{12}$. Therefore nonlocality must be small. Mathematically it means that the kernel of the RGM equations is narrow, and it is really so.

It is seen from Eqs. (3.22)–(3.24) that integration over $d^3\mathbf{r}_1$ in each term $\langle \mathbf{R}|A|\mathbf{R}'\rangle$ of the exchange kernel will lead to the substitution $\mathbf{r}_1 \to [(M+1)/2](\mathbf{R}'-\mathbf{R})+\mathbf{r}_2+\mathbf{R}$ in the atomic wave functions and to the appearance of the factor

$$\varphi_{n_1}\left\{\frac{M+1}{2}(\mathbf{R}'-\mathbf{R})+\cdots\right\}\varphi_{n_2'}\left\{\frac{M+1}{2}(\mathbf{R}'-\mathbf{R})\right\}$$

under the remaining integral over $d^3\mathbf{r}_2$. The hydrogen wave functions are $\varphi_{n_j}(\mathbf{r})_{r\to\infty} \sim \exp(-r/n_j)$. Therefore if very diffuse atomic functions are not included in the basis (say $n_{\max} < 10$, $n_{\max}$ corresponding to the most diffuse function in the basis), this factor will lead to the very rapid decrease of the exchange kernel as a function of $|\mathbf{R}-\mathbf{R}'|$ since $M/2 \simeq 10^3$. In other words, the kernel is narrow since its width

$$l_K \sim \frac{2n_{\max}}{M} \tag{4.2}$$

is very small in comparison with the characteristic atomic distances.

In fact, for narrow kernels there exists a well-developed method of moments of approximating integral operators by differential ones. It originates from the theory of stochastic processes (see, e.g., [40]) and was applied to problems similar to the present one in Refs. [21], [22], [38], and [39].

In the method of moments $g_{n_1'n_2'}(\mathbf{R}')$ under the integral in Eq. (3.13) is expanded in powers of $\Delta=\mathbf{R}'-\mathbf{R}$ in the vicinity of $\mathbf{R}'=\mathbf{R}$ retaining only several first terms.

Such a truncation is legitimate if $g_{n_1'n_2'}(\mathbf{R}')$ varies much slower than the kernel. The range of the kernel variation is given by Eq. (4.2). The range of $g_{n_1'n_2'}(\mathbf{R}')$ variation is of the order of the relative motion de Broglie wavelength $\lambda=(M\varepsilon_t)^{-1/2}$. Thus the method of moments can be used in the present problem if

$$l_K \sim n_{\max}(4\varepsilon_t/M)^{1/2} \ll 1 \ . \tag{4.3}$$

Taking into account that $1/n_{\max}$ is of the order of the characteristic velocity v_e of electrons participating in the process and $(4\varepsilon_t/M)^{1/2}$ is the relative proton velocity v_p, inequality (4.3) can be rewritten in the form

$$v_p/v_e \ll 1 \ . \tag{4.4}$$

Note that the fulfillment of this inequality is generally accepted as a justification of the conventional theory of slow atom collisions (see, e.g., [17]).

Usually only terms up to second order in Δ in the expansion of $g_{n_1'n_2'}(\mathbf{R}')$ are taken into account to get a second-order differential equation which can be physically interpreted in terms of potentials and effective masses. In the present case the third-order term must be retained, and the reason for that will become clear below. As a result we get

$$\int d^3\mathbf{R}'\langle \mathbf{R}|K|\mathbf{R}'\rangle \approx [|K^{(0)}(\mathbf{R})|]g_{n_1'n_2'}(\mathbf{R})+[|K_i^{(1)}|]\nabla_i g_{n_1'n_2'}(\mathbf{R}) + \tfrac{1}{2}[|K_{ik}^{(2)}(\mathbf{R})|]\nabla_i\nabla_k g_{n_1'n_2'}(\mathbf{R})+\tfrac{1}{6}[|K_{ijk}^{(3)}(\mathbf{R})|]\nabla_i\nabla_j\nabla_k g_{n_1'n_2'}(\mathbf{R}) \ , \tag{4.5}$$

where

$$[|K^{(0)}(\mathbf{R})|]=\int d^3\mathbf{R}'\langle \mathbf{R}|K|\mathbf{R}'\rangle \ , \tag{4.6}$$

$$[|K_i^{(1)}(\mathbf{R})|]=\int d^3\mathbf{R}'(R_i'-R_i)\langle \mathbf{R}|K|\mathbf{R}'\rangle \ , \tag{4.7}$$

$$[|K_{ik}^{(2)}(\mathbf{R})|]=\int d^3\mathbf{R}'(R_i'-R_i)(R_k'-R_k)\langle \mathbf{R}|K|\mathbf{R}'\rangle \ , \tag{4.8}$$

$$[|K_{ijk}^{(3)}(\mathbf{R})|]=\int d^3\mathbf{R}'(R_i'-R_i)(R_j'-R_j)(R_k'-R_k) \times\langle \mathbf{R}|K|\mathbf{R}'\rangle \ , \tag{4.9}$$

are the zero, first, second, and third moments of the kernel. Here and below the index notations for the three-dimensional vectors and tensors are often used together with the usual convention that the summation is to be performed over the same indices appearing twice.

B. Moments and their properties

Explicit expressions of the moments of the overlap [Eq. (3.22)], interaction [Eq. (3.24)], and kinetic energy [Eq. (3.23)] kernels are readily obtained from the general expressions (4.6)–(4.9) introducing $\Delta=\mathbf{R}'-\mathbf{R}$ as an integration variable instead of $\mathbf{R}'$. They are given in Table II.

The moments form matrices in the space of basis electronic functions. Further it will often be suitable to use operator notations $\mathbf{A}^{(0)}, \mathbf{A}_i^{(1)}, \ldots$, for these matrices. They depend on $\mathbf{R}$ and often enter different expressions together with the gradient operator ∇_i. Therefore it is suitable to use special notation $\partial_i \mathbf{A}$ for the gradient of the matrix retaining the symbol ∇_i only for gradients of the functions. In these notations we have, for example,

$$\nabla_i \mathbf{A}=\partial_i \mathbf{A}+\mathbf{A}\nabla_i \ . \tag{4.10}$$

The following general conclusions concerning the moments can be made based on the expressions in Table II:

(1) The ith moment of the overlap and interaction kernels is in some sense an average of the corresponding degree of the fluctuation $\delta\mathbf{R}^{(1),(2)}$ [see Eq. (4.1)] of the distance between atomic centers of mass due to electron exchange and therefore contain a small factor $[2/(M+1)]^i \approx (2/M)^i$; and

(2) the first three moments of the relative kinetic-energy kernel, due to the presence of derivatives in Eq. (3.23), contain terms $\sim 1/M$ and the forth moment is $\sim 1/M^2$.

As pointed out previously the nonlocal exchange kernel is hermitian and the same is true separately for the kernels of the overlap, interaction, and kinetic energy. Therefore the differential operators approximating the integral ones in the method of moments must also be hermitian. This requirement imposes relations between different moments. In the operator notations introduced above these relations are as follows ($\mathbf{A}=\mathbf{S},\mathbf{V},\mathbf{T}$):

$$\mathbf{A}^{(0)}=\mathbf{A}^{(0,0)}+\tfrac{1}{2}\partial_i \mathbf{A}_i^{(1,1)}+\tfrac{1}{4}\partial_i\partial_k \mathbf{A}_{ik}^{(2,2)}+\tfrac{1}{12}\partial_i\partial_j\partial_k \mathbf{A}_{ijk}^{(3,3)} \ , \tag{4.11}$$

$$\mathbf{A}_i^{(1)}=\mathbf{A}_i^{(1,1)}+\tfrac{1}{2}\partial_k \mathbf{A}_{ik}^{(2,2)}+\tfrac{1}{4}\partial_i\partial_j \mathbf{A}_{ijk}^{(3,3)} \ , \tag{4.12}$$

$$\mathbf{A}_{ik}^{(2)}=\mathbf{A}_{ik}^{(2,2)}+\tfrac{1}{4}\partial_j \mathbf{A}_{ijk}^{(3,3)} \ , \tag{4.13}$$

$$\mathbf{A}_{ijk}^{(3)}=\mathbf{A}_{ijk}^{(3,3)} \ . \tag{4.14}$$

TABLE II. Explicit expressions of the various moments.

Overlap and interaction kernels[a]

$$[|\mathbf{A}^{(0)}|]=\int d^3\mathbf{r}_1 d^3\mathbf{r}_2\,\mathbf{A}F(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})$$

$$[|\mathbf{A}_i^{(1)}|]=\frac{2}{M+1}\int d^3\mathbf{r}_1 d^3\mathbf{r}_2\boldsymbol{\rho}_i\,\mathbf{A}F(\mathbf{r}_1\mathbf{r}_2,\mathbf{R})$$

$$[|\mathbf{A}_{ik}^{(2)}|]=\frac{4}{(M+1)^2}\int d^3\mathbf{r}_1 d^3\mathbf{r}_2\boldsymbol{\rho}_i\boldsymbol{\rho}_k\,\mathbf{A}F(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})$$

Relative kinetic-energy kernel

$$[|\mathbf{T}^{(0)}|]=-\frac{1}{2(M+1)}\nabla^2[|\mathbf{S}^{(0)}|]$$

$$[|\mathbf{T}_i^{(1)}|]=-\frac{1}{2(M+1)}\nabla^2[|\mathbf{S}_i^{(1)}|]-\frac{1}{M+1}\nabla_i[|\mathbf{S}^{(0)}|]$$

$$[|\mathbf{T}_{ik}^{(2)}|]=-\frac{1}{M+1}\{\nabla_k[|\mathbf{S}_i^{(1)}|]+\nabla_i[|\mathbf{S}_k^{(1)}|]\}-\frac{2}{M+1}\delta_{ik}[|\mathbf{S}^{(0)}|]$$

$$[|\mathbf{T}_{ijk}^{(3)}|]=-\frac{2}{(M+1)}\{\delta_{ij}[|\mathbf{S}_k^{(1)}|]+\delta_{ik}[|\mathbf{S}_j^{(1)}|]+\delta_{jk}[|\mathbf{S}_i^{(1)}|]\}+O(1/M^3)$$

[a] $\mathbf{A}=1$ and $\mathbf{A}=V_{\text{sym}}$ [Eq. (3.27)] are to be substituted in the cases of the overlap and interaction kernels, respectively; $F(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})$ is given by Eq. (3.25).

In Eqs. (4.11)–(4.14) the matrices $\mathbf{A}^{(0,0)}$ and $\mathbf{A}_{ik}^{(2,2)}$ must be hermitian (symmetrical in the present case, when all quantities are real) and $\mathbf{A}_i^{(1,1)}$ and $\mathbf{A}_{ijk}^{(3,3)}$ must be antihermitian (antisymmetrical). These relations are the generalization for the multistate three-dimensional case of the relation between the first and the second moments considered in [39].

Note that if one connects the relations (4.11)–(4.14) with the above-stated properties of the moments concerning their dependence on $1/M$, it becomes obvious that, generally speaking, terms of different orders in powers of $1/M$ are to be taken into account to evaluate the moments. Thus, it is not enough to retain leading terms in $1/M$ in the moments, but generally speaking further terms in the expansions of the moments in powers of $1/M$ are to be included.

For the moments of the overlap and interaction kernels the expansions up to the second order in $1/M$, compatible with the relations (4.11)–(4.14), are as follows:

$$\mathbf{A}_{ik}^{(2)}=\frac{1}{M^2}\mathbf{A}_{(2)ik}^{(2,2)}\ , \tag{4.15}$$

$$\mathbf{A}_i^{(1)}=\frac{1}{M}\mathbf{A}_{(1)i}^{(1,1)}+\frac{1}{M^2}\{\mathbf{A}_{(2)i}^{(1,1)}+\tfrac{1}{2}\partial_k\mathbf{A}_{(2)ik}^{(2,2)}\}\ , \tag{4.16}$$

$$\mathbf{A}^{(0)}=\mathbf{A}_{(0)}^{(0,0)}+\frac{1}{M}\{\mathbf{A}_{(1)}^{(0,0)}+\tfrac{1}{2}\partial_i\mathbf{A}_{(1)i}^{(1,1)}\}+\frac{1}{M^2}\{\mathbf{A}_{(2)}^{(0,0)}+\tfrac{1}{2}\partial_i\mathbf{A}_{(2)i}^{(1,1)}+\tfrac{1}{4}\partial_i\partial_k\mathbf{A}_{(2)ik}^{(2,2)}\}\ . \tag{4.17}$$

For kinetic energy, analogous relations have the form

$$\mathbf{T}_{ijk}^{(3)}=\frac{1}{M^2}\mathbf{T}_{(2)ijk}^{(3,3)}\ , \tag{4.18}$$

$$\mathbf{T}_{ik}^{(2)}=\frac{1}{M}\mathbf{T}_{(1)ik}^{(2,2)}+\frac{1}{M^2}\{\mathbf{T}_{(2)ik}^{(2,2)}+\tfrac{1}{4}\partial_j\mathbf{T}_{(2)ijk}^{(3,3)}\}\ , \tag{4.19}$$

$$\mathbf{T}_i^{(1)}=\frac{1}{M}\{\mathbf{T}_{(1)i}^{(1,1)}+\tfrac{1}{2}\partial_k\mathbf{T}_{(1)ik}^{(2,2)}\}+\frac{1}{M^2}\{\mathbf{T}_{(2)i}^{(1,1)}+\tfrac{1}{2}\partial_k\mathbf{T}_{(2)ik}^{(2,2)}+\tfrac{1}{4}\partial_j\partial_k\mathbf{T}_{(2)ijk}^{(3,3)}\}\ , \tag{4.20}$$

$$\mathbf{T}^{(0)}=\frac{1}{M}\{\mathbf{T}_{(1)}^{(0,0)}+\tfrac{1}{2}\partial_i\mathbf{T}_{(1)i}^{(1,1)}+\tfrac{1}{4}\partial_i\partial_k\mathbf{T}_{(1)ik}^{(2,2)}+\frac{1}{M^2}\{\mathbf{T}_{(2)}^{(0,0)}+\tfrac{1}{2}\partial_i\mathbf{T}_{(2)i}^{(1,1)}+\tfrac{1}{4}\partial_i\partial_k\mathbf{T}_{(2)ik}^{(2,2)}+\tfrac{1}{12}\partial_i\partial_j\partial_k\mathbf{T}_{(2)ijk}^{(3,3)}\}\ . \tag{4.21}$$

In Eqs. (4.15)–(4.21) the lower index in brackets indicates the order in $1/M$. The matrices $\mathbf{A}_{(m)}^{(0,0)}$, $\mathbf{T}_{(m)}^{(0,0)}$, $\mathbf{A}_{(m)ik}^{(2,2)}$, and $\mathbf{T}_{(m)ik}^{(2,2)}$ must be hermitian and $\mathbf{A}_{(m)i}^{(1,1)}$, $\mathbf{T}_{(m)i}^{(1,1)}$, and $\mathbf{T}_{(2)ijk}^{(3,3)}$ must be antihermitian.

All the moments considered here are symmetrical tensors of the corresponding rank (see Table II). But there exists additional symmetry. Namely, it can be readily shown using explicit expressions of the moments from Table II and the fact that only spherically symmetric atomic s states are included in the basis, that in the body-fixed coordinate system $\{x'y'z'\}$ with the z' axis parallel to $\mathbf{R}$,

$$\mathbf{A}_{x'}^{(1)}=\mathbf{A}_{y'}^{(1)}=0;\quad \mathbf{A}_{z'}^{(1)}=\mathbf{A}^{(1)}(R)\ , \tag{4.22}$$

$$\mathbf{A}_{x'x'}^{(2)}=\mathbf{A}_{y'y'}^{(2)}=\mathbf{A}^{(2)\omega}(R),\quad \mathbf{A}_{z'z'}^{(2)}=\mathbf{A}^{(2)}(R)\ ,\quad \mathbf{A}_{i'k'}^{(2)}=0\ \text{ for } i'\neq k'\ . \tag{4.23}$$

In the body-fixed system, various moments are obviously functions of R only.

It is sufficient to derive explicit expressions of the ma-

trices $\mathbf{S}^{(0,0)}_{(m)}$, $\mathbf{S}^{(1,1)}_{(m)i}$, $\mathbf{S}^{(2,2)}_{(2)ik}$, $\mathbf{V}^{(0,0)}_{(m)}$, $\mathbf{V}^{(1,1)}_{(m)i}$, and $\mathbf{V}^{(2,2)}_{(2)ik}$ in order to obtain various moments with the accuracy chosen here (up to the second order in $1/M$), see Eqs. (4.15)–(4.21). These expressions are obtained by direct expansions of the integrals in Table II in powers of $1/M$ with the use of the relations (4.15)–(4.21) between different moments. The results for the moments entering the final radial equations and also for the Coulomb interaction are given in Table III.

C. General structure of the differential RGM equations

The RGM differential equations including all the terms up to the second order in $1/M$ can be written in the following form:

$$(\hat{\mathbf{W}}_3+\hat{\mathbf{W}}_2+\hat{\mathbf{W}}_1+\hat{\mathbf{W}}_0)\mathbf{g}=0 , \tag{4.24}$$

where $\mathbf{g}$ is a column vector, constructed from the functions $g_{n_1n_2}(\mathbf{R})$, and $\hat{\mathbf{W}}_j$ is the following hermitian differential operator of jth order:

$$\hat{\mathbf{W}}_3=\mathbf{B}_{ijk}\nabla_i\nabla_j\nabla_k+\tfrac{3}{2}\partial_i\mathbf{B}_{ijk}\nabla_j\nabla_k +\tfrac{3}{2}\partial_i\partial_j\mathbf{B}_{ijk}\nabla_k+\tfrac{1}{2}\partial_i\partial_j\partial_k\mathbf{B}_{ijk} , \tag{4.25}$$

$$\hat{\mathbf{W}}_2=\mathbf{D}_{ik}\nabla_i\nabla_k+\partial_i\mathbf{D}_{ik}\nabla_k+\tfrac{1}{2}\partial_i\partial_k\mathbf{D}_{ik} , \tag{4.26}$$

$$\hat{\mathbf{W}}_1=\mathbf{G}_i\nabla_i+\tfrac{1}{2}\partial_i\mathbf{G}_i , \tag{4.27}$$

$$\hat{\mathbf{W}}_0=\mathbf{U}_0+\frac{1}{M}\mathbf{U}_1+\frac{1}{M^2}\mathbf{U}_2 . \tag{4.28}$$

Expressions of all the matrices entering Eqs. (4.25)–(4.28) are given in Table IV.

The matrices $\mathbf{Q}_m$, $\mathbf{N}$, and $\boldsymbol{\varepsilon}$, which were not defined earlier, enter these expressions. The matrices $\mathbf{Q}_m$ are the "coefficients" in the expansion of the matrix $\mathbf{Q}$ of the Coulomb integrals (3.19) in powers of $1/M$:

$$\mathbf{Q}=\mathbf{Q}_0+\frac{1}{M}\mathbf{Q}_1+\frac{1}{M^2}\mathbf{Q}_2 . \tag{4.29}$$

In the present simplified model when only even spherically symmetric atomic states are taken into account $\mathbf{Q}_1$ vanishes identically.

The normalization matrix $\mathbf{N}$ is defined by the relation

$$\mathbf{N}=\mathbf{I}+\mathbf{S}^{(0,0)}_{(0)} , \tag{4.30}$$

where $\mathbf{I}$ is a unit matrix and $\boldsymbol{\varepsilon}$ is a matrix of atomic energies defined by the relations

$$[n_1n_2|\boldsymbol{\varepsilon}|n_1'n_2']=(\varepsilon_{n_1}+\varepsilon_{n_2})\delta_{n_1n_1'}\delta_{n_2n_2'} . \tag{4.31}$$

The RGM equation [Eq. (4.24)] which is yet very

TABLE III. Expressions in the form of quantum-chemical integrals of the Coulomb interaction and various moments entering radial differential RGM equations (5.1). All the integrations are performed in the body-fixed coordinate system (x',y',z') with the z' axis parallel to $\mathbf{R}$; in this system $\mathbf{R}=(0,0,R)$.

	Coulomb interaction, hermitian matrix[a]
	$[\lvert\mathbf{Q}_0\rvert]=\int d^3\mathbf{r}_1'd^3\mathbf{r}_2'\varphi_{n_1}(\mathbf{r}_1')\varphi_{n_2}(\mathbf{r}_2')\mathbf{V}^{(0)}(\mathbf{r}_1',\mathbf{r}_2',\mathbf{R})\varphi_{n_1'}(\mathbf{r}_1')\varphi_{n_2'}(\mathbf{r}_2')$
	Zero-order moments, hermitian matrices[b]
Overlap	$[\lvert\mathbf{S}^{(0,0)}_{(0)}\rvert]=\int d^3\mathbf{r}_1'd^3\mathbf{r}_2'F_0(\mathbf{r}_1',\mathbf{r}_2',\mathbf{R})$
	$[\lvert\mathbf{S}^{(0,0)}_{(1)}\rvert]=3[\lvert\mathbf{S}^{(0,0)}_{(0)}\rvert]$
Interaction[c]	$[\lvert\mathbf{V}^{(00)}_{(0)}\rvert]=\int d^3\mathbf{r}_1'd^3\mathbf{r}_2'\mathbf{V}^{(0)}_{\mathrm{sym}}(\mathbf{r}_1',\mathbf{r}_2',\mathbf{R})F_0(\mathbf{r}_1',\mathbf{r}_2',\mathbf{R})$
	$[\lvert\mathbf{V}^{(0,0)}_{(1)}\rvert]=2[\lvert\mathbf{V}^{(0,0)}_{(0)}\rvert]$
	First-order moments, antihermitian matrices
Overlap	$[\lvert\mathbf{S}^{(1,1)}_{(1)}\rvert]=2\int d^3\mathbf{r}_1'd^3\mathbf{r}_2'(z_1'-z_2'-R)F_0(\mathbf{r}_1',\mathbf{r}_2',\mathbf{R})$
Interaction[c]	$[\lvert\mathbf{V}^{(1,1)}_{(1)}\rvert]=2\int d^3\mathbf{r}_1'd^3\mathbf{r}_2'(z_1'-z_2'-R)\mathbf{V}^{(0)}_{\mathrm{sym}}(\mathbf{r}_1',\mathbf{r}_2',\mathbf{R})F_0(\mathbf{r}_1',\mathbf{r}_2',\mathbf{R})$
	Second-order moments, hermitian matrices
Overlap	$[\lvert\mathbf{S}^{(2,2)}_{(2)}\rvert]=4\int d^3\mathbf{r}_1'd^3\mathbf{r}_2'(z_1'-z_2'-R)^2F_0(\mathbf{r}_1,\mathbf{r}_2',\mathbf{R})$
Interaction[c]	$[\lvert\mathbf{V}^{(2,2)}_{(2)}\rvert]=4\int d^3\mathbf{r}_1'd^3\mathbf{r}_2'(z_1'-z_2'-R)^2\mathbf{V}^{(0)}_{\mathrm{sym}}(\mathbf{r}_1',\mathbf{r}_2',\mathbf{R})F_0(\mathbf{r}_1,\mathbf{r}_2,\mathbf{R})$

[a] $\mathbf{V}^{(0)}(\mathbf{r}_1',\mathbf{r}_2',\mathbf{R})=\dfrac{1}{R}+\dfrac{1}{[\mathbf{r}_1'-\mathbf{r}_2'-\mathbf{R}|}-\dfrac{1}{|\mathbf{r}_1'-\mathbf{R}|}-\dfrac{1}{|\mathbf{r}_2'-\mathbf{R}|}$.

[b] $F_0(\mathbf{r}_1',\mathbf{r}_2',\mathbf{R})=\varphi_{n_1}(\mathbf{r}_1')\varphi_{n_2}(\mathbf{r}_2')\varphi_{n_1'}(\mathbf{r}_2'+\mathbf{R})\varphi_{n_2'}(\mathbf{r}_1'-\mathbf{R})$.

[c] $\mathbf{V}^{(0)}_{\mathrm{sym}}(\mathbf{r}_1',\mathbf{r}_2',\mathbf{R})=\dfrac{1}{R}+\dfrac{1}{|\mathbf{r}_1'-\mathbf{r}_2'-\mathbf{R}|}-\tfrac{1}{2}\left[\dfrac{1}{r_1'}+\dfrac{1}{r_2'}+\dfrac{1}{|\mathbf{r}_1'-\mathbf{R}|}+\dfrac{1}{|\mathbf{r}_2'+\mathbf{R}|}\right]$.

TABLE IV. Matrices entering Eqs. (4.24)–(4.28).

Hermitian matrices

$$\mathbf{D}_{ik}=-\frac{1}{M}\mathbf{N}\delta_{ik}+\frac{1}{M^2}\{\tfrac{1}{2}\mathbf{V}^{(2,2)}_{(2)ik}+\tfrac{1}{4}[(\boldsymbol{\varepsilon}-E\mathbf{I})\mathbf{S}^{(2,2)}_{(2)ik}+\mathbf{S}^{(2,2)}_{(2)ik}(\boldsymbol{\varepsilon}-E\mathbf{I})]$$
$$-3\mathbf{S}^{(0,0)}_{(0)}\delta_{ik}+\mathbf{N}\delta_{ik}\}\ ;$$

$$\mathbf{U}_0=\mathbf{Q}_0+\mathbf{V}^{(0,0)}_{(0)}+\tfrac{1}{2}(\boldsymbol{\varepsilon}\mathbf{N}+\mathbf{N}\boldsymbol{\varepsilon})\ ;$$

$$\mathbf{U}_1=\mathbf{V}^{(0,0)}_{(1)}+\tfrac{1}{2}[(\boldsymbol{\varepsilon}-E\mathbf{I})\mathbf{S}^{(0,0)}_{(1)}+\mathbf{S}^{(0,0)}_{(1)}(\boldsymbol{\varepsilon}-E\mathbf{I})]-\tfrac{1}{2}(\boldsymbol{\varepsilon}\mathbf{N}+\mathbf{N}\boldsymbol{\varepsilon})\ ;$$

$$\mathbf{U}_2=\mathbf{Q}_2+\mathbf{V}^{(0,0)}_{(2)}+\tfrac{1}{2}[(\boldsymbol{\varepsilon}-E\mathbf{I})\mathbf{S}^{(0,0)}_{(2)}+\mathbf{S}^{(0,0)}_{(2)}(\boldsymbol{\varepsilon}-E\mathbf{I})]-\tfrac{1}{2}(\boldsymbol{\varepsilon}\mathbf{S}^{(0,0)}_{(1)}+\mathbf{S}^{(0,0)}_{(1)}\boldsymbol{\varepsilon})$$
$$+\tfrac{1}{2}(\boldsymbol{\varepsilon}\mathbf{N}+\mathbf{N}\boldsymbol{\varepsilon})$$

Antihermitian matrices

$$\mathbf{B}_{ijk}=-\frac{1}{6M^2}(\delta_{ij}\mathbf{S}^{(1,1)}_{(1)k}+\delta_{ik}\mathbf{S}^{(1,1)}_{(1)j}+\delta_{jk}\mathbf{S}^{(1,1)}_{(1)i})\ ;$$

$$\mathbf{G}_i=\frac{1}{M}\{\mathbf{V}^{(1,1)}_{(1)i}+\tfrac{1}{2}[(\boldsymbol{\varepsilon}-E\mathbf{I})\mathbf{S}^{(1,1)}_{(1)i}+\mathbf{S}^{(1,1)}_{(1)i}(\boldsymbol{\varepsilon}-E\mathbf{I})]$$
$$+\frac{1}{M^2}\{\mathbf{V}^{(1,1)}_{(2)i}+\tfrac{1}{2}[(\boldsymbol{\varepsilon}-E\mathbf{I})\mathbf{S}^{(1,1)}_{(2)i}+\mathbf{S}^{(1,1)}_{(1)i}(\boldsymbol{\varepsilon}-E\mathbf{I})]-\tfrac{1}{2}(\boldsymbol{\varepsilon}\mathbf{S}^{(1,1)}_{(1)i}+\mathbf{S}^{(1,1)}_{(1)i}\boldsymbol{\varepsilon})\}$$

different from the equations used in conventional theory can, in principle, be used to solve the collision problem in the adopted electronic basis. However, our present aim is to come as close as possible to the conventional formulation retaining only the leading corrections due to both taking into account the finite value of the nuclear mass and the indistinguishability of electrons.

In order to obtain equations in a form close to the familiar Schrödinger equations, further simplifications and transformations are needed. First of all, some simplifications may be made in the operators $\hat{\mathbf{W}}_j$. If we want to take into account only first corrections to the conventional picture then the term $(1/M^2)\mathbf{U}_2$ can safely be neglected in $\hat{\mathbf{W}}_0$ which is the analog of the potential matrix. More than that, all $\sim 1/M^2$ potential-like terms which will arise below from the differential operators under R-dependent transformations of the equations can also be neglected. But the $\sim 1/M^2$ term in $\mathbf{D}_{ik}$ must be retained. It is just this term which leads to the modification of the reduced mass of the relative motion. The operator $\hat{\mathbf{W}}_1$ has no analog in the conventional picture. Therefore, only leading $\sim 1/M$ terms will be retained in it and in other operators with analogous structure (including antihermitian matrices).

V. NONADIABATIC RADIAL SCHRÖDINGER EQUATIONS IN THE MOLECULAR BASIS

A. Radial differential RGM equations

The above-described simplifications do not change the general form of equations which remain different from the familiar Schrödinger equations in the molecular basis. To get this form further transformations are needed.

The tensor structure of the operators $\hat{\mathbf{W}}_j$ is such that they are invariant under rotations in space. Since electronic angular momenta of the atoms in the presently adopted basis are zero, this invariance means that the relative angular momentum $\hat{\boldsymbol{l}}$ is conserved (the corresponding quantum number is l). Then, using the standard procedure, the following radial equations for the column vector $\mathbf{g}^l(R)$ are obtained:

$$(\hat{\mathbf{W}}^R_3+\hat{\mathbf{W}}^R_2+\hat{\mathbf{W}}^R_1+\hat{\mathbf{W}}^R_0)\mathbf{g}^l(R)=0\ . \tag{5.1}$$

The radial hermitian differential operators $\hat{\mathbf{W}}^R_j$ are as follows:

$$\hat{\mathbf{W}}^R_3=-\frac{1}{2M^2}\left[\mathbf{S}^{(1,1)}_{(1)}\frac{d^3}{dR^3}+\tfrac{3}{2}d\mathbf{S}^{(1,1)}_{(1)}\frac{d^2}{dR^2}\right.$$
$$\left.+\tfrac{3}{2}d^2\mathbf{S}^{(1,1)}_{(1)}+\tfrac{1}{2}d^3\mathbf{S}^{(1,1)}_{(1)}\right]\ , \tag{5.2}$$

$$\hat{\mathbf{W}}^R_2=\mathbf{D}^R\frac{d^2}{dR^2}+d\mathbf{D}^R\frac{d}{dR}+\tfrac{1}{2}d^2\mathbf{D}\ , \tag{5.3}$$

with

$$\mathbf{D}^R=-\frac{1}{M}\mathbf{N}+\frac{1}{M^2}\{\tfrac{1}{2}\mathbf{V}^{(2,2)}_{(2)}$$
$$+\tfrac{1}{4}[(\boldsymbol{\varepsilon}-E\mathbf{I})\mathbf{S}^{(2,2)}_{(2)}+\mathbf{S}^{(2,2)}_{(2)}(\boldsymbol{\varepsilon}-E\mathbf{I})]$$
$$-3\mathbf{S}^{(0,0)}_{(0)}+\mathbf{N}\}\ , \tag{5.4}$$

$$\hat{\mathbf{W}}^R_1=\mathbf{G}^R\frac{d}{dR}+\tfrac{1}{2}d\mathbf{G}^R\ , \tag{5.5}$$

with

$$\mathbf{G}^R=\frac{1}{M}\{\mathbf{V}^{(1,1)}_{(1)}+\tfrac{1}{2}[(\boldsymbol{\varepsilon}-E\mathbf{I})\mathbf{S}^{(1,1)}_{(1)}+\mathbf{S}^{(1,1)}_{(1)}(\boldsymbol{\varepsilon}-E\mathbf{I})]\}\ , \tag{5.6}$$

$$\hat{\mathbf{W}}^R_0=\mathbf{U}_0-\mathbf{N}E+\frac{1}{M}\mathbf{U}^R_1\ , \tag{5.7}$$

with

$$\mathbf{U}_1^R=\mathbf{U}_1+\frac{l(l+1)}{R^2}\mathbf{N}\ , \tag{5.8}$$

and $\mathbf{U}_0$ and $\mathbf{U}_1$ are given in Table IV. In accord with the above-introduced notation for the gradient of the matrix [see Eq. (4.10)] the notation $d\,\mathbf{A}$ is used for the matrix $d\,\mathbf{A}/dR$ in these equations and below.

Expressions of all the matrices entering $\hat{\mathbf{W}}_j$ in the form of quantum-chemical integrals are given in Table III.

Because the basis functions are orthogonal for $R\to\infty$ (all $\mathbf{S}^{(i,i)}_{(m)R\to\infty}\to\mathbf{0}$), Eq. (5.1) is to be solved with the usual boundary conditions (see the discussion of this point in Refs. [33] and [35]):

$$g^l_{n_1'n_2'}(R)_{R\to 0}\to 0\ , \tag{5.9}$$

and, in the case of scattering,

$$g^l_{n_1'n_2'}(R)_{R\to\infty}\sim \exp\left[-i\left[kR-\frac{l\pi}{2}\right]\right]\delta_{n_1n_1'}\delta_{n_2n_2'} -S^l_{n_1'n_2',n_1n_2}\exp\left[i\left[k'R-\frac{l\pi}{2}\right]\right] \tag{5.10}$$

with

$$k=\left\{(M+1)\left[E-(\varepsilon_{n_1}+\varepsilon_{n_2})\left[1-\frac{1}{M}\right]\right]\right\}^{1/2}\ ,$$
$$k'=\left\{(M+1)\left[E-(\varepsilon_{n_1'}+\varepsilon_{n_2'})\left[1-\frac{1}{M}\right]\right]\right\}^{1/2}\ . \tag{5.11}$$

In the case of energetically open channels,

$$g^l_{n_1'n_2'}(R)_{R\to\infty}\sim\exp(-|k'|R)\ . \tag{5.12}$$

In the case of energetically closed channels and in the case of bound states

$$g^l_{n_1'n_2'}(R)_{R\to\infty}\to 0\ . \tag{5.13}$$

Scattering cross sections are expressed through the elements $S^l_{n_1'n_2',n_1n_2}$ of the scattering matrix in the usual way (see, e.g., [16,17]).

B. Orthonormalization of the RGM equations Schrödinger radial equations in the molecular basis

To make the radial differential equations (5.1) as similar as possible to the conventional radial Schrödinger equations let us introduce a new column vector $\boldsymbol{\eta}^l(R)$ by the relation

$$\mathbf{g}^l(R)=\mathbf{N}^{-1/2}\boldsymbol{\eta}^l(R) \tag{5.14}$$

and multiply Eq. (5.1) by $\mathbf{N}^{-1/2}$ from the left. Then one obtains the following equations for $\boldsymbol{\eta}^l(R)$:

$$\left[-\frac{1}{M}\frac{d^2}{dR^2}\mathbf{I}+\frac{l(l+1)}{MR^2}+\mathbf{U}_0^N-E\mathbf{I}\right]\boldsymbol{\eta}^l=-\left[\mathbf{U}_1^N+\mathbf{G}^{R,N}\frac{d}{dR}+\tfrac{1}{2}d\mathbf{G}^{R,N}\right]\boldsymbol{\eta}^l-\left[\mathbf{D}_2^{R,N}\frac{d^2}{dR^2}+d\mathbf{D}_2^{R,N}\frac{d}{dR}\right]\boldsymbol{\eta}^l +\frac{1}{2M^2}\left[\mathbf{S}^{(1,1)N}_{(1)}\frac{d^3}{dR^3}+\tfrac{3}{2}d\mathbf{S}^{(1,1)N}_{(1)}\frac{d^2}{dR^2}+\tfrac{3}{2}d^2\mathbf{S}^{(1,1)N}_{(1)}\frac{d}{dR}\right]\boldsymbol{\eta}^l\ . \tag{5.15}$$

Here,

$$\mathbf{U}_0^N=\mathbf{N}^{-1/2}\mathbf{U}_0\mathbf{N}^{-1/2}\ , \tag{5.16}$$

$$\mathbf{U}_1^N=\mathbf{N}^{-1/2}\mathbf{U}_1\mathbf{N}^{-1/2}+\frac{1}{2M}[d\mathbf{N}^{-1/2}d\mathbf{N}^{1/2}+d\mathbf{N}^{1/2}d\mathbf{N}^{-1/2}]+\tfrac{1}{2}[\mathbf{N}^{-1/2}\mathbf{G}^R d\mathbf{N}^{-1/2}-d\mathbf{N}^{-1/2}\mathbf{G}^R\mathbf{N}^{-1/2}]\ , \tag{5.17}$$

$$\mathbf{G}^{R,N}=\mathbf{N}^{-1/2}\mathbf{G}^R\mathbf{N}^{-1/2}\ , \tag{5.18}$$

$$\mathbf{D}_2^{R,N}=\frac{1}{M^2}\{\tfrac{1}{2}\mathbf{N}^{-1/2}\mathbf{V}^{(2,2)}_{(2)}\mathbf{N}^{-1/2}-3\mathbf{N}^{-1/2}\mathbf{S}^{(0,0)}_{(0)}\mathbf{N}^{-1/2}+\tfrac{1}{4}\mathbf{N}^{-1/2}[(\boldsymbol{\varepsilon}-E\mathbf{I})\mathbf{S}^{(2,2)}_{(2)}+\mathbf{S}^{(2,2)}_{(2)}(\boldsymbol{\varepsilon}-E\mathbf{I})]\mathbf{N}^{-1/2}+\mathbf{I} -\tfrac{1}{4}[\mathbf{N}^{-1/2}\mathbf{S}^{(1,1)}_{(1)}d\mathbf{N}^{-1/2}-d\mathbf{N}^{-1/2}\mathbf{S}^{(1,1)}_{(1)}\mathbf{N}^{-1/2}]\}\ , \tag{5.19}$$

$$\mathbf{S}^{(1,1)N}_{(1)}=\mathbf{N}^{-1/2}\mathbf{S}^{(1,1)}_{(1)}\mathbf{N}^{-1/2}\ . \tag{5.20}$$

Again, insignificant from the point of view considered at the end of Sec. IV, the terms $\sim 1/M^2$ were omitted.

Since $\mathbf{N}=\mathbf{I}+\mathbf{S}^{(0,0)}_{(0)}$, where $\mathbf{S}^{(0,0)}_{(0)}$ (see Table III) is the usual two-electron overlap matrix of quantum chemistry,

$$\mathbf{N}_{R\to\infty}\to\mathbf{I}\ , \tag{5.21}$$

and the boundary conditions for $\boldsymbol{\eta}^l(R)$ are the same as the boundary conditions (5.9)–(5.13) for $\mathbf{g}^l(R)$.

Note that the orthonormalizing transformation (5.14) was considered in quantum chemistry in connection with the solution of the secular equations written in a nonorthogonal basis (see, e.g., [41,42]) and was discussed

in connection with the RGM equations in nuclear physics (see, e.g., [33,35,37]).

Neglecting the rhs of Eq. (5.15), the remaining equations coincide exactly with the usual radial equations written in the basis of orthonormalized products of atomic wave functions. The rhs describes the corrections due to the simultaneous accounting for the indistinguishability of electrons and finite value of the nuclear mass. The terms $\sim 1/M$ include corrections to the interaction matrix ($\mathbf{U}_1^{(N)}$) and dynamical coupling ($\mathbf{G}^{R,N}$) due to the exchange fluctuations of the distance between the atomic centers of mass. The last two terms $\sim 1/M^2$ will give the fluctuational contribution to the effective reduced mass in the radial equations in the molecular basis.

An introduction of this basis is necessary to decouple maximally the equations because $\mathbf{U}_0^N$ has large nondiagonal elements. In the basis of products of the atomic wave functions, the adiabatic electronic terms are obtained as solutions of the following eigenvalue equations:

$$(\mathbf{U}_0 - U\mathbf{N})\mathbf{a} = 0 \ . \tag{5.22}$$

After the transformation

$$\mathbf{a} = \mathbf{N}^{-1/2}\mathbf{b} \tag{5.23}$$

and multiplication of Eq. (5.22) from the left by $\mathbf{N}^{-1/2}$ one obtains

$$(\mathbf{U}_0^N - U)b = 0 \ . \tag{5.24}$$

The diagonalization of $\mathbf{U}_0^N$ provides a set of adiabatic electronic terms

$$\mathbf{\Omega}\mathbf{U}_0^N\mathbf{\Omega}^+ = \mathbf{U}_{\rm mol} \tag{5.25}$$

corresponding to the adopted basis. Here, $\mathbf{\Omega}$ is a unitary transformation matrix and $\mathbf{U}_{\rm mol}$ is a diagonal matrix

$$[\beta|\mathbf{U}_{\rm mol}|\beta'] = \delta_{\beta\beta'}U_\beta \ , \tag{5.26}$$

where U_β are the molecular potential curves and β is a set of quantum numbers characterizing molecular adiabatic states.

Let us now introduce a new set of radial functions χ^l,

$$\eta^l = \mathbf{\Omega}^+\chi^l \ , \tag{5.27}$$

substitute Eq. (5.27) into Eq. (5.15), and multiply from the left by $\mathbf{\Omega}$.

Then we obtain the radial equations in the molecular basis for the singlet states

$$\left[-\frac{1}{M}\mathbf{I}\frac{d^2}{dR^2} + \frac{l(l+1)}{MR^2}\mathbf{I} + \mathbf{U}_{\rm mol} - E\mathbf{I}\right]\chi^l = -\left[\mathbf{V}_{\rm mol} + \mathbf{G}_{\rm mol}\frac{d}{dR} + \tfrac{1}{2}d\mathbf{G}_{\rm mol}\right]\chi^l + \left[\delta\mathbf{M}^{-1}\frac{d^2}{dR^2} + d\,\delta\mathbf{M}^{-1}\frac{d}{dR}\right]\chi^l \ , \tag{5.28}$$

where

$$\mathbf{V}_{\rm mol} = \mathbf{\Omega}\mathbf{U}_1^N\mathbf{\Omega}^+ + \frac{1}{M}d\mathbf{\Omega}d\mathbf{\Omega}^+ + \tfrac{1}{2}[\mathbf{\Omega}\mathbf{G}^{R,N}d\mathbf{\Omega}^+ - d\mathbf{\Omega}\mathbf{G}^{R,N}\mathbf{\Omega}^+] \ , \tag{5.29}$$

$$\mathbf{G}_{\rm mol} = \mathbf{\Omega}\mathbf{G}^{R,N}\mathbf{\Omega}^+ - \frac{2}{M}\mathbf{\Omega}d\mathbf{\Omega}^+ \ , \tag{5.30}$$

and $\delta\mathbf{M}^{-1}$ is a diagonal matrix

$$[\beta|\delta\mathbf{M}^{-1}|\beta'] = \delta_{\beta\beta'}\delta M_\beta^{-1} \tag{5.31}$$

with

$$\delta M_\beta^{-1} = -[\beta|D_{2,\rm mol}|\beta] \ , \tag{5.32}$$

$$\mathbf{D}_{2,\rm mol} = \mathbf{\Omega}\mathbf{D}_2^{R,N}\mathbf{\Omega}^+ - \frac{1}{4M^2}[\mathbf{\Omega}\mathbf{S}_{(1)}^{(1,1)N}d\mathbf{\Omega}^+ - d\mathbf{\Omega}\mathbf{S}_{(1)}^{(1,1)N}\mathbf{\Omega}^+] \ . \tag{5.33}$$

Equations for the triplet states have the same form as Eq. (5.28), only the signs must be changed before the exchange terms.

Note that Eqs. (5.28)–(5.33) are the main result of this paper.

In the present homonuclear case, $\mathbf{\Omega}$ does not approach $\mathbf{I}$ as $R \to \infty$ because even and odd molecular states conserve their character everywhere. But the modification of the boundary conditions (5.10) due to this effect can be readily obtained (see, e.g., [17]) and will not be considered here.

VI. ILLUSTRATION: NONADIABATIC HEITLER-LONDON APPROXIMATION (NAHLA)

As mentioned in the Introduction the present investigation was stimulated to a considerable degree by the difficulties with the heavy-particle reduced mass in the problems of the supercold hydrogen atoms collisions [6] and highly excited vibrational states of H_2 [20]. In both problems distances between nuclei considerably exceeding equilibrium are of importance. But at such distances the interaction between the atoms is weak enough.

Therefore the electronic structure can be at least qualitatively correctly described within the basis consisting of antisymmetrized products of the ground-state hydrogen wave functions. In the conventional adiabatic theory it is the famous Heitler-London approximation (HLA), (see, e.g., [43]). It is natural to call the radial equation obtained by the method of the present paper in the same electronic basis the nonadiabatic Heitler-London approximation (NAHLA).

It seems to us useful to consider NAHLA in more detail. Comparison of NAHLA and HLA will allow us to better understand the difference between the mass dependent corrections in the present nonadiabatic approach and the conventional adiabatic one. Except that at large enough distances NAHLA allows us to estimate the correction to the reduced mass mentioned in the Introduction.

A. Radial Schrödinger equation in NAHLA

Introducing simplified notations for the integrals from Table III

$$\begin{aligned} &S^2=[|\mathbf{S}_{(0)}^{(0,0)}|]; \quad N=1+S^2 , \\ &Q=[|\mathbf{Q}_0|] , \\ &I=[|\mathbf{V}_{(0)}^{(00)}|] , \\ &S_2^{(2)}=[|\mathbf{S}_{(2)}^{(2,2)}|] , \\ &V_2^{(2)}=[|\mathbf{V}_{(2)}^{(2,2)}|] . \end{aligned} \tag{6.1}$$

Equation (5.28) for $l=0$ reduces in NAHLA to the form

$$\left[-\frac{d}{dR}\frac{1}{M_{\text{eff}}}\frac{d}{dR}+\frac{Q+I}{1+S^2}-\varepsilon_t\right]\chi+U_1^N\chi=0 , \tag{6.2}$$

with $\chi=\chi^0$ where the correction to the potential is given by

$$U_1^N=\frac{2I-3\varepsilon_t S^2-\frac{1}{4}N^{-1}(dN/dR)^2}{MN} \tag{6.3}$$

and an inverse effective mass is as follows:

$$\frac{1}{M_{\text{eff}}}=\frac{1}{M}-\frac{1}{M^2}\frac{V_2^{(2)}-\varepsilon_t S_2^{(2)}+2N-6S^2}{2N} . \tag{6.4}$$

It is seen that if one neglects the second-order correction to the inverse mass and the first-order correction to the potential, Eq. (6.2) would reduce to that obtained in HLA.

The correction to the reduced mass principally cannot be obtained within conventional theory. But the first-order correction to the potential in $1/M$, the so-called adiabatic correction $U_{1\,\text{ad}}$, can be calculated. In the present case of the axially symmetric electronic state, it is defined in the body-fixed coordinate frame as an average over the electronic state of the operator

$$H'=-\frac{1}{M}\frac{\partial^2}{\partial R^2}-\frac{1}{4M}(\nabla_{\mathbf{r}_1^c}+\nabla_{\mathbf{r}_2^c})^2+\frac{1}{MR^2}(\hat{\mathbf{l}}_1+\hat{\mathbf{l}}_2)^2 \tag{6.5}$$

(see, e.g., [44]). Here $\hat{\mathbf{l}}_1=-i[\mathbf{r}_1^c\nabla_{\mathbf{r}_1^c}]$, $\hat{\mathbf{l}}_2=-i[\mathbf{r}_2^c\nabla_{\mathbf{r}_2^c}]$ are the operators of the electronic orbital angular momenta, $\mathbf{r}_1^c$ and $\mathbf{r}_2^c$ are radii vectors from the geometrical center between protons and electrons, and the partial differentiation $\partial^2/\partial R^2$ is performed at a constant $\mathbf{r}_1^c$ and $\mathbf{r}_2^c$.

If

$$\begin{aligned} \psi^{\text{HL}}=N^{-1/2}[&\varphi(\mathbf{r}_1^c+\tfrac{1}{2}\mathbf{R})\varphi(\mathbf{r}_2^c-\tfrac{1}{2}\mathbf{R}) \\ &+\varphi(\mathbf{r}_1^c-\tfrac{1}{2}\mathbf{R})\varphi(\mathbf{r}_2^c+\tfrac{1}{2}\mathbf{R})] \end{aligned} \tag{6.6}$$

is used for the adiabatic electronic wave function, then

$$U_{1\text{ad}}^{\text{HL}}=\int d^3\mathbf{r}_1^c d^3\mathbf{r}_2^c\psi^{\text{HL}}H'\psi^{\text{HL}}=\frac{1}{M}+\delta U_{\text{ad}}^{\text{HL}} , \tag{6.7}$$

where

$$\delta U_{\text{ad}}^{\text{HL}}=\frac{-\frac{1}{4}N^{-1}(dN/dR)^2-S^2+T(R)}{MN} \tag{6.8}$$

and

$$\begin{aligned} T(R)=\int d^3\mathbf{r}_1^c d^3\mathbf{r}_2^c&\varphi(\mathbf{r}_1^c+\tfrac{1}{2}\mathbf{R})\varphi(\mathbf{r}_2^c-\tfrac{1}{2}\mathbf{R}) \\ &\times\left[\frac{1}{R^2}(\hat{\mathbf{l}}_1+\hat{\mathbf{l}}_2)^2-\tfrac{1}{4}(\nabla_{\mathbf{r}_1^c}+\nabla_{\mathbf{r}_2^c})^2\right] \\ &\times\varphi(\mathbf{r}_1^c-\tfrac{1}{2}\mathbf{R})\varphi(\mathbf{r}_2^c+\tfrac{1}{2}\mathbf{R}) . \end{aligned} \tag{6.9}$$

The first constant term $1/M$ in Eq. (6.7) is nothing else but a first-order correction for the finite values of the proton masses to the ground-state energy of two noninteracting hydrogen atoms. Therefore, from the present point of view, it is to be included in the definition of zero energy and only $\delta U_{\text{ad}}^{\text{HL}}$, which goes to zero for $R\to\infty$, is to be compared with U_1^N as shown in Eq. (6.3). It is seen that the difference is significant.

The energy-dependent terms which are present in U_1^N [Eq. (6.3)] and $1/M_{\text{eff}}$ [Eq. (6.4)] are often insignificant from the practical point of view. The thing is that energy-dependent terms enter U_1^N and $1/M_{\text{eff}}$ in such a way that a significant variation of the latter will be achieved in intervals of the ε_t variation of the order of 1 a.u. Considering, e.g., thermal atomic collisions or highly excited vibrational states, when $|\varepsilon_t|$ does not exceed $\sim 10^3$ K ($\sim 10^{-2}$ a.u.), these energy-dependent terms can be safely neglected in U_1^N and $1/M_{\text{eff}}$.

The corrections U_1^N and $\delta U_{\text{ad}}^{\text{HL}}$ are of the same order and both of them lead to a small modification of zero order in the $1/M$ Heitler-London adiabatic potential. The inaccuracy of HLA is, of course, much larger than U_1^N and $\delta U_{\text{ad}}^{\text{HL}}$. Therefore we shall not consider the corrections to the potential in more detail.

For the reduced mass the situation is different. In conventional theory there is no modification of this mass which in all approximations is equal to the reduced mass of the protons. The present nonadiabatic theory predicts such a modification and it may be expected that the correction to $1/M$ calculated in the present NAHLA correctly describes this effect at least in distances large enough so that the influence of the excited states may be neglected.

B. Effective mass in NAHLA. Results and discussion

One obtains from Eq. (6.4), neglecting the energy-dependent term, the following expressions for the effective masses of both singlet (S) and triplet (T) states:

$$M_{\text{eff}}^{S,T}=M+1+\delta M^{S,T}(R) \tag{6.10}$$

with

$$\delta M^{S,T}=\pm\frac{V_2^{(2)}-6S^2}{2(1\pm S^2)} . \tag{6.11}$$

Here, the plus sign corresponds to the singlet state and the minus sign to the triplet state.

The results of the numerical calculation of δM^S and δM^T at $R>3$ a.u. are given in Fig. 2. The details concerning the evaluation of the integral $V_2^{(2)}$ can be found in the Appendix. The calculations were not performed for smaller R because there the Heitler-London electronic basis is obviously very bad.

It is seen from Fig. 1 that $\delta M^{S,T}\to 0$ as $R\to\infty$ and is, therefore, in accord with the physical intuition that $M_{\text{eff}}^{S,T}$ goes to the atomic mass $M+1$. At not very large R the corrections $\delta M^{S,T}$ may become of the order of unity (see Fig. 2). But it is important to note that δM^S and δM^T have opposite signs. It is the manifestation of the purely exchange nature of the modification of the reduced mass of atoms. This effect cannot be understood in terms of classical physics as it has been said in Ref. [20] "there will be some nonadiabatic lag of the electrons behind the nuclei as they vibrate."

Nevertheless, since $V_2^{(2)}$ appears to be negative, $M_{\text{eff}}^S<M+1$ in agreement with the semiempirical fit in [20]. But, generally speaking, it can become smaller than M at distances smaller than those considered here. Of course, it is difficult to compare directly the curve in Fig. 2 with the value obtained semiempirically in [20], $\delta M^S=-0.075$. There are two reasons for this.

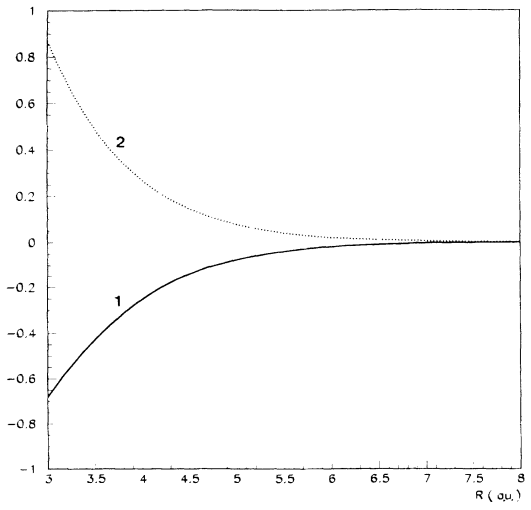

FIG. 2. Mass corrections $\delta M^{S,T}$ [Eq. (6.11)]. (1) $X\,{}^1\Sigma_g^+$ state; (2) $a\,{}^3\Sigma_u^+$ state.

First of all, the vibrational problem with $M_{\text{eff}}^S(R)$ is to be considered. But it needs the knowledge of $\delta M^S(R)$ for smaller R where the Heitler-London basis is obviously bad.

The second reason is that in performing the solution of the vibrational problem, the correction U_1^N to the adiabatic electronic potential calculated within the theory developed here is to be used but not the adiabatic correction $U_{1\,\text{ad}}$ of the conventional theory.

The present nonadiabatic theory allows us to solve both problems provided the results of the calculations of the adiabatic electronic states are expressed in terms of the electronic basis constructed from the orthonormalized products of atomic wave functions. The recent consideration of the H_2 ground electronic state within the generalized valence-bond method in [45] may be useful in this respect.

The following is also to be noted. The extension of the electronic basis will give corrections to U_1^N and δM^S which themselves are small corrections to the adiabatic electronic potential and M. Therefore, the influence of the dimension of the basis used for the adiabatic calculations upon final results through δM^S and U_1^N may be expected to be much weaker than through the adiabatic electronic potential itself. Such a situation was mentioned in [46] in connection with the calculations of the conventional adiabatic correction to the electronic potential-energy curves.

VII. GENERAL DISCUSSION

The radial equations in the molecular basis [Eq. (5.28)] solve principally the problem formulated in the Introduction. They have a form almost similar to the conventional scattering equations in the molecular basis. The left-hand side (lhs) of Eq. (5.28) is a familiar set of equations of radial nuclear motion in the fields of adiabatic electronic potentials $U_\beta(R)$.

The rhs includes two terms possessing direct analogues in the conventional formulation. The first one $(1/M)d\boldsymbol{\Omega}\,d\boldsymbol{\Omega}^+$ [see Eq. (5.29)] corresponds to the so-called adiabatic correction to the interaction and the second one $-(2/M)\boldsymbol{\Omega}\,d\boldsymbol{\Omega}^+$ [see Eq. (5.30)] corresponds to radial nonadiabatic coupling. But, contrary to the conventional formulation they go to zero fast enough as $R\to\infty$. In fact, these terms coincide with the conventional adiabatic correction to the interaction and radial nonadiabatic coupling if the latter is calculated assuming that the orthonormalized atomic basis is a strictly diabatic basis.

All other terms on the rhs of Eq. (5.28), except those arising from the isotope shifts of the atomic energies and the trivial difference between $1/(M+1)$ and $1/M$ in Eq. (3.13), are due to the exchange fluctuations of the distance between atomic centers of mass. The most important of them are the fluctuational radial nonadiabatic coupling $\boldsymbol{\Omega}\mathbf{G}^{R,N}\boldsymbol{\Omega}^+$ [see Eq. (5.30)] and the fluctuational R-dependent contribution to the inverse reduced-mass corrections δM_β^{-1}. All these fluctuational contributions go exponentially to zero as $R\to\infty$. In particular, due to this $\delta M_\beta^{-1}\underset{R\to\infty}{\to}-1/M^2$, reproducing the reduced mass of

atoms in the scattering equations at large R.

Two additional comments are to be made concerning the fluctuational terms in Eq. (5.28).

First, in the regions of close pseudocrossings of the molecular potential curves corresponding to $-(2/M)\Omega\, d\Omega^{+}$, nonadiabatic coupling between such terms will be anomalously large and very near to the conventional nonadiabatic coupling matrix elements. Fluctuational nonadiabatic coupling is not affected by pseudocrossing and remains small. Therefore, in such regions the corrections to the standard theory of nonadiabatic transitions from the effects considered here are expected to be insignificant (see the discussion in [17], Chap. 2, Sec. 3).

The second comment concerns the energy dependence present in the fluctuational terms. It appears there due to the fact that the transformation (5.14) excludes nonorthogonality only in zero order in $1/M$. Therefore, the functions η^{l} [Eq. (5.14)] and χ^{l} [Eq. (5.27)] can literally be understood as wave functions of relative motion only if this energy dependence is neglected. An explicit account of this dependence leads to nonorthogonality of the relative motion wave functions corresponding to different E. But the total electron-nuclear wave functions Ψ [Eq. (3.9)] corresponding to different E will be, of course, orthogonal (see the discussion of this question in [34]). This fact reminds us that $\mathbf{R}$ is not a dynamical variable in the usual quantum-mechanical sense. It is a collective variable describing the simultaneous motion of nuclei and electrons. From a practical point of view this energy dependence may often be insignificant. The structure of the fluctuational terms is such that the range of their energy variation is ~ 1 a.u.

VIII. CONCLUSIONS

The following general conclusions can be made.

(1) The inequality $1/M \ll 1$ plays a double role. First, due to this inequality, the fluctuations $\mathbf{R}^{(1)} \leftrightarrows \mathbf{R}^{(2)}$ of the distance between the centers of mass caused by the electron exchange are small (but not slow). Second, this inequality leads to high frequencies of the transitions between adiabatic electronic states in comparison with the frequencies of nuclear motion.

(2) Derivation of the atomic motion equations in the molecular basis which are compatible with the correct boundary conditions includes two physically distinct steps. The first step is the derivation of the local equations including the slow collective variable $\mathbf{R}$ by averaging over the fast but small exchange fluctuations $\mathbf{R}^{(1)} \leftrightarrows \mathbf{R}^{(2)}$. The second step is the transformation of these local equations to the adiabatic electronic basis, where the equations can be approximately decoupled due to the large differences between electronic and nuclear frequencies. Just this second step corresponds to the adiabatic approximation in its classical sense.

(3) For the practical realization of the present approach, it is most suitable to perform quantum-chemical calculations of the adiabatic electronic states directly in the nonorthogonal atomic basis. Such calculations provide a large amount of necessary information: overlap matrices and transformation matrices from the orthonormalized atomic basis to the molecular basis. Only molecular integrals for the higher moments of the overlap and interaction are to be calculated additionally. In the usual molecular-orbital approach, an additional procedure is needed to extract this information from the adiabatic electronic wave functions. This problem is similar to the analysis of the molecular-orbital wave functions in terms of the valence-bond wave functions (see, e.g., [47]).

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APPENDIX

Two integrals, S^2 and $V_2^{(2)}$ [Eq. (6.1), and Table III], are to be evaluated to obtain the mass correction $\delta M^{S,T}$ [Eq. (6.11)].

(a) Overlap integral S^2.

$$S^2 = e^{-2R}(1+R+R^2/3)^2 \,. \tag{A1}$$

(b) Interaction integral $V_2^{(2)}$.

With the internuclear axis chosen as the z axis this integral reduces to the form

$$V_2^{(2)} = 4\int d^3\rho_1 d^3\rho_2 (\rho_{z1}+\rho_{z2})^2 \times \left\{ \frac{1}{R} - \frac{1}{\rho_1} - \frac{1}{\rho_2} + \frac{1}{|\boldsymbol{\rho}_1+\boldsymbol{\rho}_2|} \right\} \times \varphi(\boldsymbol{\rho}_1)\varphi(\boldsymbol{\rho}_2)\varphi(\boldsymbol{\rho}_2+\mathbf{R})\varphi(\boldsymbol{\rho}_1-\mathbf{R}) \,, \tag{A2}$$

where ρ_{z1} and ρ_{z2} are the z components of $\boldsymbol{\rho}_1$ and $\boldsymbol{\rho}_2$ and $\varphi(\boldsymbol{\rho}) = (1/\sqrt{\pi})e^{-\rho}$ is the ground-state hydrogen wave function.

After performing analytically the integration of the first three terms in Eq. (A2), $V_2^{(2)}$ may be written in the following form:

$$V_2^{(2)} = 4(I_2 + I_3 - 2I_1) \tag{A3}$$

with

$$I_1 = \tfrac{1}{30} e^{-2R}(45+90R+71R^2+32R^3+9R^4+\tfrac{4}{3}R^5) \tag{A4}$$

and

$$I_2=\frac{2}{R}e^{-2R}(1+R+\tfrac{1}{3}R^2)(1+R+\tfrac{9}{20}R^2+\tfrac{7}{60}R^3+\tfrac{1}{60}R^4)\ . \tag{A5}$$

The integral I_3 which corresponds to the interelectronic interaction term in Eq. (A2) has been evaluated numerically using prolate spheroidal coordinates ($1\le\lambda<\infty$, $-1\le\mu\le 1$, $0\le\varphi\le 2\pi$) through the following formula:

$$I_3=\frac{R^7}{16}\sum_{l=0}^{3}(2l+1)I_3^{(l)} \tag{A6}$$

with

$$\begin{aligned}I_3^{(l)}=&\int_1^{\infty}d\lambda_2 Q_l^0(\lambda_2)e^{-R\lambda_2}\\&\times\int_{-1}^{1}d\mu_2 P_l^0(\mu_2)(\lambda_2^2-\mu_2^2)\\&\times\int_1^{\lambda_2}d\lambda_1 P_l^0(\lambda_1)e^{-R\lambda_1}\\&\times\int_{-1}^{1}d\mu_1 P_l^0(\mu_1)(\lambda_1^2-\mu_1^2)(\lambda_1\mu_1-\lambda_2\mu_2)^2\ ,\end{aligned} \tag{A7}$$

where P_l^0 and Q_l^0 are Legendre functions of the first and second kind, respectively.

These fourfold integrals have been performed numerically using the program QB01A of Harwell Library with a Gauss-Legendre procedure.

[1] J. Weiner, F. Masnou-Seeuws, and A. Giusti-Suzor, Adv. Atom. Mol. Opt. Phys. **26**, 209 (1990), and references therein.
[2] D. Sesko, T. Walker, C. Monroe, A. Gallaher, and C. Wieman, Phys. Rev. Lett. **63**, 961 (1989).
[3] H. R. Thorsheim, Y. Wang, and J. Weiner, Phys. Rev. A **41**, 2873 (1990).
[4] H. A. J. Meijer, Z. Phys. D **17**, 257 (1990).
[5] R. W. Heather and P. S. Julienne, Phys. Rev. A **47**, 1887 (1993).
[6] B. J. Verhaar, J. M. Koelman, H. T. Stoof, O. J. Luiten, and S. B. Crampton, Phys. Rev. A **35**, 3825 (1987).
[7] J. M. Koelman, S. B. Crampton, H. T. Stoof, O. J. Luiten, and B. J. Verhaar, Phys. Rev. A **38**, 3535 (1988).
[8] A. C. Moan, E. Tiesinga, H. T. Stoof, and B. J. Verhaar, Physica B **165/166**, 17 (1990).
[9] E. Tiesinga, H. T. Stoof, and B. J. Verhaar, Physica B **165/166**, 19 (1990).
[10] C. Lhuiler, J. Phys. (Paris) **44**, 1 (1983).
[11] A. Hershcovitch, Phys. Rev. Lett. **63**, 750 (1989).
[12] M. J. Janieson, A. Dalgarno, and J. N. Yukich, Phys. Rev. A **46**, 6956 (1992).
[13] W. Kolos and L. Wolniewicz, J. Chem. Phys. **49**, 404 (1968).
[14] W. Kolos and L. Wolniewicz, Chem. Phys. Lett. **24**, 457 (1974).
[15] W. Kolos, K. Szalewicz, and H. J. Monkhorst, J. Chem. Phys. **84**, 3278 (1986).
[16] N. F. Mott and H. S. W. Massey, *The Theory of Atomic Collisions* (Oxford University Press, Oxford, 1965).
[17] E. E. Nikitin and S. Ya. Umanskii, *Theory of Slow Atomic Collisions* (Springer, Berlin, 1984).
[18] R. G. Woley and B. T. Sutcliffe, Chem. Phys. Lett. **45**, 393 (1977).
[19] H. J. Monkhorst, Phys. Rev. A **36**, 1544 (1987).
[20] B. R. Bunker, C. J. McLarnon, and R. E. Moss, Mol. Phys. **33**, 425 (1977).
[21] J. A. Wheeler, Phys. Rev. **52**, 1083 (1937); **52**, 1107 (1937).
[22] J. B. Delos, Rev. Mod. Phys. **53**, 287 (1981).
[23] J. B. Delos, Phys. Rev. A **23**, 2301 (1981).
[24] A. Macias and A. Riera, Phys. Rep. **90**, 301 (1982).
[25] M. Kimura and N. F. Lane, Adv. Atom. Molec. Opt. Phys. **26**, 80 (1990).
[26] R. T. Pack and J. O. Hirshfelder, J. Chem. Phys. **52**, 4198 (1970).
[27] A. Riera and A. Salin, J. Phys. B **9**, 2877 (1976).
[28] L. I. Ponomarev, S. I. Vinitsky, and F. R. Vukailovich, J. Phys. B **13**, 847 (1980).
[29] M. H. Mittleman and H. Tai, Phys. Rev. A **8**, 1880 (1973).
[30] R. P. Bunker and R. E. Moss, Mol. Phys. **33**, 417 (1977).
[31] D. M. Bishop and S. K. Shih, J. Chem. Phys. **64**, 162 (1976).
[32] J. Y. Park, W. Scheid, and W. Greiner, Phys. Rev. C **6**, 1565 (1972).
[33] C. W. Wong, Phys. Rep. **15**, 283 (1974).
[34] K. Wildermuth and Y. C. Tang, *A Unified Theory of the Nucleus* (Vieweg, Braunschweig, 1977).
[35] H. Friedrich, Phys. Rep. **74**, 209 (1981).
[36] Y. C. Tang, in *Topics in Nuclear Physics II*, edited by T. T. S. Kuo and S. S. M. Wong, Lecture Notes in Physics, Vol. 145 (Springer, Berlin-Heidelberg, 1981).
[37] T. Fliessbach and H. Walliser, Nucl. Phys. A **377**, 84 (1982).
[38] R. E. Peierls and J. Yoccoz, Proc. Phys. Soc. London Ser. A **70**, 381 (1957).
[39] B. Banerjee and D. M. Brink, Z. Phys. **258**, 46 (1973).
[40] N. van Kampen, *Stochastic Processes in Physics and Chemistry* (North Holland, Amsterdam, 1981).
[41] P. O. Löwdin, Adv. Quant. Chem. **5**, 185 (1970).
[42] G. A. Gallup, R. L. Vance, J. R. Collins, and J. M. Norbeck, Adv. Quant. Chem. **16**, 229 (1982).
[43] C. A. Coulson, *Valence* (Oxford Univ. Press, New York, 1961).
[44] W. Kolos, Adv. Quant. Chem. **5**, 99 (1970).
[45] W. Cencek, J. Komasa, and J. Rychlewski, J. Chem. Phys. **95**,2572 (1991).
[46] D. M. Bishop and L. M. Cheung, Adv. Quant. Chem. **12**, 1 (1980).
[47] P. C. Hiberty, Int. J. Quant. Chem. **XIX**, 259 (1981).