

Long-range effects in three-particle molecular systems

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A transcendental equation is obtained for the effective interaction of the two heavy particles in a system consisting of one light and two heavy particles. A special feature of the derivation of this equation is the allowance for repulsion at small distances, which makes it possible to consider real three-particle systems. The He_2^- system is taken as an example. © 1996 American Institute of Physics. [S1063-7761(96)00103-0]

1. INTRODUCTION

The dynamics of three bodies in quantum mechanics exhibits entirely new physical properties manifesting themselves in effects unusual from the standpoint of the two-body problem. One is the Efimov effect, which appears because of long-range terms in the effective interaction in the hyper-radius of the system¹ or in the relative Jacobi coordinate between one particle and the remaining pair.² This long-range r^{-2} interaction is restricted to the region¹⁾

$$r_0 \ll r \ll 1/|\kappa|, \quad (1)$$

where r_0 is the characteristic range of pairwise interactions, and κ is the wave number of the bound state (for $\kappa > 0$) or the virtual state (for $\kappa < 0$; the pole of the scattering amplitude on the unphysical sheet). When the range is infinite, i.e., when $\kappa \rightarrow 0$, there is logarithmic crowding of the levels in the three-particle spectrum, a direct manifestation of the Efimov effect. Real systems are, unfortunately, in conditions differing greatly from such a marked long-range effect, which nevertheless determines to a greater or lesser extent the dynamics of real three-particle systems.¹

An interesting area of such three-particle dynamics could be the physics of diatomic negative molecular ions, in particular, their asymptotic part of the spectrum, which in view of the small scale of the electron-atom coupling energy (affinity) and large distances is determined by the mechanisms of three-particle dynamics. It appears³ that in a system consisting of one light and two heavy particles with short-range pairwise potentials, the asymptotic part of the effective interaction may contain both the Efimov long-range interaction term¹ of the r^{-2} type and a term of the r^{-1} type. For pairwise coupling energies ε corresponding to real physical objects, the bound-state spectrum of a three-particle system is determined by the r^{-1} component. This long-range coupling between the heavy particles is caused by the interaction between the light particle and a heavy particle and is restricted to the region (1), as in the Efimov effect. At large distances the decreasing power law is replaced by an exponential law for real bound states in pairs or is restricted to the region $\sim |\kappa^{-1}|$ for a virtual state.

Here the pairwise interaction is added to the effective potential generated by the light particle (we call the latter an exchange interaction). When the region (1) is large, i.e., when the pairs are weakly coupled, the generated spectrum

corresponds to weakly-bound states with large rms radii, which makes it possible to ignore the details of the pairwise interaction between the particles. However, the binding energies of real atom-atom and electron-atom systems are not so low, and therefore one must take into account the behavior of their pairwise potentials.

In Ref. 3 the pairwise interaction was chosen in the form of separable Yamaguchi potentials. Hence the results of that paper cannot be directly applied in the analysis of real systems of the atom-electron-atom type (except for unique systems with an especially low real coupling of an electron and an atom of the Zn^- type, where $\varepsilon \approx -0.1$ eV; see Ref. 4). It is not that realistic potentials in the attraction region are unlike the Yamaguchi potential: such a potential can easily be fitted to describe both the bound state and the scattering parameters generated by the attraction region of real physical systems. The problem is that realistic potentials must contain a gigantic (in comparison to the attraction region) repulsive core (see, e.g., Ref. 5), whose behavior cannot be described by a separable potential. On the other hand, the height of this core is several orders of magnitude greater than the depth of the attractive part of the potential. Therefore we are justified to formulate a spectral problem with a pairwise potential of the electron-atom interaction $V(r)$ in the following form:

$$V(r) = \infty, \quad r < R, \quad V(r) = v(r), \quad r \geq R, \quad (2)$$

where R is the repulsion radius (in what follows we call this potential a "wall"), and $v(r)$ is a shallow attractive potential. In particular, we can take $v(r)$ in the separable form $\nu(r)\nu(r')$ of the Yamaguchi type (its shape is defined in Sec. 2), obviously restricting its action to the region outside the wall, i.e., assuming that $\nu(r) = 0$ for $r < R$. Here it is proper to note that the full form of the potential energy operator $v(\mathbf{r}, \mathbf{r}')$ can reduce either to $v(\mathbf{r}, \mathbf{r}') = v(r)\delta(\mathbf{r} - \mathbf{r}')$, with a local potential $v(r)$, or to a separable potential $v(\mathbf{r}, \mathbf{r}') = \nu(r)\nu(r')$. Since in what follows we examine the energy region in which the electron wavelength is much larger than atomic dimensions, the pairwise electron-atom interaction can be restricted to the S -wave.

In this case we can easily describe the behavior of the interaction cross section of a pair both at low momenta (two parameters in the Yamaguchi potential) and at relatively high momenta, at least to the first unitary limit, since the phase of elastic scattering by the wall in the S wave is simply $-kR$, where \mathbf{k} is the momentum of the pair's relative motion. The

simplicity of such a description is achieved by the fact that for $V(r)$ in the form (2) the phases of scattering by the wall and by the Yamaguchi potential are added.

Having assessed the feasibility of describing pairwise interaction in this manner, we now formulate the problem of the interaction of two atoms via an exchange electron with a fairly realistic pairwise potential. Here, however, we must deal with the problem of three-particle interaction with an unusual combination of a potential and the boundary condition at the wall.

In this paper we derive a transcendental equation for the effective potential of the interaction of two identical atoms that emerges because of the third particle in the system, the electron. We take the electron-atom potential in the form (2) and assume the atoms to be structureless.

An example considered in this paper is the He_2^- system. In particular, we show that the existing experimental data indicate that the long-range region is large and, as a result, a negative molecular ion He_2^- exists even when there are no bound states in the He^- and He_2 systems. The recent discovery⁶ of a helium dimer only strengthens the above statement.

2. THE TWO-BODY PROBLEM

Here we consider the problem of two bodies with a reduced mass m interacting via a compound potential of the type (2). The following statements are straightforward: the two-body pairwise wave function Ψ is zero for $r \leq R$, its product with the pairwise potential (2) in this region is also zero, and the first derivative Ψ' with respect to the radial coordinate exhibits a discontinuity at $r=R$. To verify these statements, we only need to examine solutions with a finite repulsive potential that tends to infinity in the positive-energy region $E = k_0^2/2m$.

Introducing the notation v_∞ for the finite value of the wall potential, and $F(r)/r$ and $G(r)/r$ for the regular and irregular solutions in the field of potential v , which behave like $\sin(k_0 r)/k$ and $\cos(k_0 r)/k$ as $r \rightarrow \infty$ (the Wronskian is zero), we write the leading terms in the solution of the Schrödinger equation for $v_\infty \rightarrow \infty$ as

$$\Psi \rightarrow \frac{1}{\sqrt{2mv_\infty} \sqrt{F^2(R) + G^2(R)}} \exp(\sqrt{2mv_\infty}(r-R)), \quad r < R,$$

$$\Psi \rightarrow \frac{F(r)G(R) - F(R)G(r)}{\sqrt{F^2(R) + G^2(R)}}, \quad r \geq R.$$

The above statements follow directly from these asymptotic expressions.

Thus, the Schrödinger equation with potential (2) has the standard form

$$-\frac{1}{2m} \Delta \Psi + v \Psi - E \Psi = 0,$$

with an additional boundary condition $\Psi(R) = 0$. In addition, the infinitely high wall (in the sense of a limit; see above) introduces a discontinuity into the first derivatives at the boundary.

We solve this simple equation in a rather roundabout way so as not to return to the same problems in the three-body problem. We start with the problem of bound states with energy $\varepsilon = -\kappa^2/2m$. Let us take the Fourier transform of the Schrödinger equation. Since the first derivative is discontinuous at $r=R$, the Fourier transform of the Laplacian acquires an additional term in the form of an integral over the surface of a sphere of radius R :

$$\mathcal{F}[\Delta \Psi] = -k^2 \Psi(k) - I(k),$$

$$I = \int_{r=R} \exp(i\mathbf{k}\mathbf{r}) \Psi' R^2 d\Omega.$$

This produces an additional term in the Lippmann-Schwinger equation:

$$\Psi = g_0(\varepsilon) v \Psi + \frac{1}{2m} g_0(\varepsilon) I.$$

Here $g_0(z) = (z - k^2/2m)^{-1}$ is the free Green's function in the momentum representation. To use the boundary conditions, we go back to the coordinate representation. We introduce the notation $g_0(x, y)$ for the Green's function in this representation. To economize on space, we use primed symbols for the arguments of the Green's function that are involved in three-dimensional integration. Moreover, since we are interested only in the S -wave, in what follows we do not introduce special notation for partial harmonics. With this system of notation the equation for the wave function assumes the following form:

$$\Psi(r) = g(r, r') v \Psi + g(r, R) \frac{4\pi R^2}{2m} \Psi'(R).$$

By allowing for the boundary condition $\Psi(R) = 0$ we eliminate the derivative and obtain a two-particle integral equation for the effective Green's function $g_{\text{eff}}(x, y)$ responsible for the boundary condition at the wall:

$$\Psi(r) = g_{\text{eff}}(r, r') v \Psi, \quad (3)$$

$$g_{\text{eff}}(x, y) = g_0(x, y) - \frac{g_0(x, R) g_0(R, y)}{g_0(R, R)}.$$

Equation (3) can easily be solved for any short-range potential and becomes especially simple for separable potentials. Here we consider a Yamaguchi potential $v(x, y) = \nu(x) \nu(y)$ (in the coordinate representation) with a range that extends from R to infinity, and write the potential in the form of projection operators $|\nu\rangle\langle\nu|$, assuming in this case three-dimensional integration over all space with the three-dimensional ball of radius R excluded. It is convenient to write the Yamaguchi potential in the form

$$\nu(x) \nu(y) = \frac{N}{xy} \exp(-\beta x) \exp(-\beta y), \quad (4)$$

where β is the potential's parameter, which determines the range of the forces, and N is a coupling constant.

We can now solve Eq. (3) by simple projection on $\langle\nu|$, which leads to the following spectral equation:

$$1 = \langle\nu| g_{\text{eff}} |\nu\rangle. \quad (5)$$

This expression can be thought of either as an equation for κ with N fixed or as an equation for the coupling constant at fixed energy. Here we find the coupling constant N by fixing the pair's energy. Simple integration results in

$$N = -\frac{(\beta + \kappa)^2 \beta}{4\pi m} \exp(2\beta R), \quad (6)$$

which differs only by an exponential factor from the expression for the coupling constant of a potential defined over the entire range.

The shape of the wave function for the Yamaguchi potential follows directly from Eq. (3), where it is simpler to find the quantity $\langle \nu | \Psi \rangle$ from the normalization condition. This wave function (for $r \geq R$)

$$\Psi(r) = \sqrt{\frac{\kappa}{2\pi} \frac{\beta(\beta + \kappa)}{(\beta - \kappa)^2}} \frac{\exp[-\beta(r - R)] - \exp[-\kappa(r - R)]}{r}$$

with $\kappa \ll \beta$ coincides with the wave function of the weakly-bound state for any short-range potential (see, e.g., Ref. 7) in the region $\beta(r - R) \gg 1$, differing from the wave function in the potential without a core only in the shift of the active region by the repulsion radius. This is especially evident for probability densities, or $|\Psi|^2 d^3r$, which differ only in a shift by R and, therefore have the same normalization.

The scattering problem can be solved as simply as the above problem. Denoting the Green's function in the range of positive energies $E = k_0^2/2m + i0$ by $g_0^+(x, y)$ and proceeding in the same manner as above, we arrive at a reduced equation for the wave function of the scattering state Ψ^+ in any partial harmonic:

$$\Psi^+(r) = \Psi_0(r) - \frac{g_0^+(r, R)}{g_0^+(R, R)} \Psi_0(R) + g_{\text{eff}}^+ \Psi. \quad (7)$$

Here $g_{\text{eff}}^+(x, y)$ is determined in the same way as for negative energies, and Ψ_0 is the respective partial harmonic of the plane wave.

The method of solving Eq. (7) is similar to the method for the discrete spectrum. For applications we will need the scattering cross section. Hence here we only outline the scheme for finding the partial amplitude. After projecting on $\langle \nu |$ we find the quantity $\langle \nu | \Psi \rangle$, substitute its value into the wave function, and determine the factor in front of the diverging wave in the asymptotic region. The factor is the partial harmonic of the S -wave. This is the way in which the elastic scattering phase δ_{tot} (or the amplitude) is found. In particular, substituting the undetermined value of the coupling constant N and fixing the pole in the scattering amplitude at $k_0 = i\kappa$, i.e., determining the real level for $\kappa > 0$ or the virtual level for $\kappa < 0$, we obtain the coupling constant, which coincides with (6). A remarkable feature of the composite potential (2) is the additivity of the scattering phases at the wall, δ_∞ , and the scattering phase for the Yamaguchi potential, δ_y , in which now there is no wall radius R (it is hidden in the definition of κ):

$$\begin{aligned} \delta_{\text{tot}} &= \delta_\infty + \delta_y, \\ \delta_\infty &= -k_0 R, \end{aligned} \quad (8)$$

$$\tan \delta_y = \frac{2\beta k_0 (\beta + \kappa)^2}{(\beta^2 + k_0^2)^2 - (\beta^2 - k_0^2)(\beta + \kappa)^2}.$$

Concluding the study of the problem of two bodies with a composite potential (2), we note that it is convenient to use an equation like (3) in describing real systems at low energies. Note that an "exact" numerical solution of the equations in integral or differential form for realistic potentials in atomic physics is entirely out of the question if only because the accuracy needed to properly account for the exponentially increasing and exponentially decreasing terms in the repulsion region is determined by an exponential with a decrement of three or more orders of magnitude (for Morse-type potentials). Naturally, such accuracy is not needed for physical systems, since the uncertainty of the pairwise potentials is much higher. In real calculations we must either "cut off" the core at reasonable heights in the integral equations or impose a zero boundary condition at the core in the differential form, i.e., we automatically distort the "realistic" potential. Hence it is reasonable to introduce a scheme in which experimental data are used to determine the parameters of a composite potential like (2) with a wall (not necessarily with attraction in separable form), while equations like (3) or (7), which are free of the numerical problem of cancellation of large terms, are used in applications.

3. THE THREE-BODY PROBLEM

Here we examine the problem of three interacting particles, two of which (1 and 2) are identical and have mass M , and the third has mass μ , with $\mu \ll M$. Such a mass ratio and the type of potentials chosen presupposes the existence of a system consisting of two atoms and a single electron (although not necessarily), and below we speak of atoms when referring to the heavy particles and of an electron when referring to the light particle. This system has a wave function that is either even or odd under permutations of the spatial coordinates of the pair of atoms. The method is valid in both cases. Here we consider systems with even wave functions.

Below we use coordinates and potentials with subscripts denoting a pair of particles: the subscript i denotes a pair with the absent particle i . For instance, V_3 and r_3 refers to the pair of particles 1 and 2, i.e., to the atoms. With such notation the potential V_3 may be of an arbitrary type (we choose the Morse potential), while the potentials V_1 and V_2 between the atoms and the electron are chosen in the form (2).

For the canonical system of coordinates we take the Jacobi coordinates ρ_i between particle i and the center of mass of the remaining pair, and r_i , between the particles in the pair. The possible ways in which the system can be broken into pairs yield three sets of Jacobi coordinates, related to each other by linear transformations. For instance,

$$\begin{aligned} r_1 &= \rho_3 + \frac{r_3}{2}, & \rho_1 &= -\frac{\mu}{\mu + M} \rho_3 + \frac{1}{2} \frac{\mu + 2M}{\mu + M} r_3; \\ r_2 &= \rho_3 - \frac{r_3}{2}, & \rho_2 &= -\frac{\mu}{\mu + M} \rho_3 - \frac{1}{2} \frac{\mu + 2M}{\mu + M} r_3. \end{aligned}$$

Earlier³ the Faddeev equations were used to obtain, via the semiclassical approximation, the potential for the heavy particles in a system consisting of two heavy and one light particles coupled only by Yamaguchi potentials between a heavy particle and the light particle. It turned out that aside from slight differences, this expression coincides with the one obtained earlier by Fonseca *et al.*⁸ directly from the Schrödinger equation in the Born–Oppenheimer approximation. Here we immediately use the leading term in the series expansion of the Schrödinger equation in powers of μ/M . This part is called the Born–Oppenheimer approximation in methods of expansion in the two-center basis (see, e.g., Ref. 9).

The physical reason for the possibility of variable separation in a three-particle equation in this limit is more than obvious: with $\mu/M \rightarrow 0$ the heavy particle ceases to move in relation to the center of mass of the electron–atom pair. Hence the coordinate r_3 becomes canonical in all sets of Jacobi coordinates, which makes it possible to separate the variables.

To verify the above statement, we note that the three-particle wave function Ψ can be written in terms of an arbitrary pair of Jacobi coordinates, $\Psi(\rho_1, r_1) \equiv \Psi(\rho_2, r_2) \equiv \Psi(\rho_3, r_3)$, and for $\mu/M \rightarrow 0$ with allowance for the relationship between the sets of coordinates we get

$$\Psi(\rho_3, r_3) = \Psi(-r_3, r_2) = \Psi(r_3, r_1).$$

To economize on space, instead of writing the set of coordinates in full we place a subscript on the wave function, i.e., $\Psi(\mathbf{x}, \mathbf{r}_i) \equiv \Psi_i$ and assume that the absence of Faddeev equations here will exclude any mix-up with the notation for the components of the wave function in the Faddeev reduction process.

With such notation the Schrödinger equation of the system with $\mu/M \ll 1$ assumes the form

$$-\frac{1}{2\mu}\Delta_{\rho_3}\Psi_3 - \frac{1}{M}\Delta_{r_3}\Psi_3 + V_3(r_3)\Psi_3 + V_2(r_2)\Psi_2 + V_1(r_1)\Psi_1 = E\Psi_3, \quad (9)$$

where the reduced electron mass in relation to the pair, i.e. $m_{3,12}$, is replaced by the electron mass. Otherwise we would exceed the available accuracy and have an effective potential with incorrect asymptotic behavior. Below we demonstrate this directly. The potentials V_1 and V_2 are chosen in the form (2). Their attractive part is still denoted by $v_i(x, y) = v_i(x)v_i(y)$ with the appropriate subscript. Here we assume that the pairwise interaction of the electron and an atom is contained only in the S -wave.

In examining a specific problem we will not do all calculations with an arbitrary potential; rather, for greater clarity we deal with a separable potential. For instance the result of a potential acting on a wave function can be written as follows:

$$v_1\Psi_1 = v_1(r_1)f(\mathbf{r}_3), \quad v_2\Psi_2 = v_2(r_2)f(-\mathbf{r}_3),$$

where $f(\mathbf{x}) = \langle v(r)\Psi(\mathbf{x}, r) \rangle$, and the angle brackets stand for integration over all space except for a ball of radius R . Here $f(\mathbf{x})$ is an even function.

Next we take the Fourier transform with respect to the variable ρ_3 to Eq. (9). The Fourier transforms of the terms with potential energy are straightforward,

$$\mathcal{F}[v_1\Psi_1] = \exp(i\mathbf{k}\mathbf{r}_3/2)v(k)f(\mathbf{r}_3),$$

$$\mathcal{F}[v_2\Psi_2] = \exp(-i\mathbf{k}\mathbf{r}_3/2)v(k)f(\mathbf{r}_3),$$

and we will not discuss them here any further. However, transformation of the Laplacian in ρ_3 requires a more thorough study. As in the two-particle problem, to the standard term $-k^2\Psi_3(k, \mathbf{r}_3)$ we must add two terms, I_1 and I_2 , in the form of integrals over two spheres: one of radius R encompasses the first atom, and the other the second. For the first term we show that after we go over to the first set of Jacobi coordinates, the expression

$$I_1 = \int \exp(-i\mathbf{k}\rho_3)\nabla_{\rho_3}\Psi_3 dS$$

acquires an especially simple form, which when we take into account only the S -wave interaction in coordinate r_1 becomes

$$I_1 = \frac{4\pi R}{k} \exp\left(\frac{i\mathbf{k}\mathbf{r}_3}{2}\right) \sin(kR)\Psi'_1(\mathbf{r}_3, R).$$

The prime denotes the derivative with respect to r_1 , i.e., $\Psi'_1(\mathbf{r}_3, R) = \partial\Psi_1(\mathbf{r}_3, R)/\partial R$. The expression for the integral over the second sphere differs in \mathbf{r}_3 being replaced by $-\mathbf{r}_3$. Hence below we allow for the fact that the wave function is even and write the derivative at the boundary without a subscript.

Defining the function $U(r_3)$, which we call the effective potential, by the relationship

$$-\frac{1}{M}\Delta_{r_3}\Psi(k, \mathbf{r}_3) + V_3(r_3)\Psi(k, \mathbf{r}_3) - E\Psi(k, \mathbf{r}_3) = -U(r_3)\Psi(k, \mathbf{r}_3) \quad (10)$$

and introducing the notation

$$G(k; U) = \frac{\exp(i\mathbf{k}\mathbf{r}_3/2) + \exp(-i\mathbf{k}\mathbf{r}_3/2)}{U - k^2/2\mu},$$

we arrive at the Lippmann–Schwinger equation with an additional term:

$$\Psi_3 = G(k; U) \left[v(k)f(\mathbf{r}_3) + \frac{2\pi R}{k\mu} \sin(kR)\Psi' \right],$$

which is similar to the equation for the two-particle problem in Sec. 2. The approach to this equation is the same as the one used in the two-particle problem.

We go to the ρ_3 -representation by an inverse Fourier transform and shift to the first set of Jacobi coordinates to be able to use the boundary condition:

$$\Psi(\mathbf{r}_3, r_1) = G(r_1, r'_1) \{ v(r'_1) \} f(\mathbf{r}_3) + \frac{2\pi R^2}{\mu} G(r_1, R) \Psi',$$

$$G(x, y) = \int \frac{\sin(kx)}{kx} \exp\left(\frac{i\mathbf{k}\mathbf{r}_3}{2}\right) G(k; U) \frac{\sin(ky)}{ky} \frac{d^3k}{(2\pi)^3}.$$

At $r_1=R$ the wave function vanishes, which makes it possible to eliminate the derivative (see Eq. (3)) and arrive at the spectral equation

$$1 = \langle \nu(r') | G_{\text{eff}}(r', r'') | \nu(r'') \rangle, \quad (11)$$

$$G_{\text{eff}}(x, y) = G(x, y) - \frac{G(x, R)G(R, y)}{G(R, R)},$$

for $U(r_3)$, an equation that formally coincides with Eq. (5) in the two-particle problem. The difference lies in the presence of an additional term in the Green's function reflecting the effect of the second atom.

Thus, the variables in the Schrödinger equation have separated. First in the spectral problem (11) we determine the function $U(r_3)$, and then solve Eq. (10) where this function acts as a local-potential addition to V_3 . Below we employ graphical means to illustrate the behavior of the effective potential.

4. THE EFFECTIVE POTENTIAL

In this section we give the expressions for the terms of the transcendental equation (10) for the effective potential and study some features of the effective potential related to the presence of repulsion in the electron-atom system at small distances.

We introduce the notation $u = \sqrt{-2\mu U(r_3)}$ ($\text{Re } u > 0$). Obtaining an equation for u only requires evaluating a somewhat cumbersome integral with allowance for the definition of the Yamaguchi potential, its range of action (Eqs. (2) and (4)), and the normalization condition (6). Here we give the final expressions in the regions $r_3 < 2R$ and $r_3 \geq 2R$, which appear in calculations and involve some interesting physics: attraction suddenly changes its behavior when electrons are unable to pass "between" atoms. The expressions are cumbersome, so to shorten notation we introduce the following column within braces:

$$\begin{Bmatrix} g_1 \\ g_2 \end{Bmatrix} = \begin{cases} g_1(r_3), & r_3 < 2R, \\ g_2(r_3), & r_3 \geq 2R. \end{cases}$$

At $r_3 = 2R$ the functions g_1 and g_2 coincide, with the result that the expressions given below are continuous over the entire range $0 \leq r_3 < \infty$.

The components of the implicit function needed to determine $u(r_3)$ can be written as follows:

$$G(R, R) = -\frac{\mu}{2\pi R^2 u} \left[\sinh(Ru) \exp(-uR) + \frac{1}{r_3 u} \begin{Bmatrix} g_1 \\ g_2 \end{Bmatrix} \right], \quad (12)$$

$$g_1 = \frac{1}{2} [1 - \exp(-ur_3) - \sinh(ur_3) \exp(-2uR)],$$

$$g_2 = \sinh^2(uR) \exp(-ur_3);$$

$$\langle \nu | G(r', R) | \nu \rangle = -A \left[\frac{\sinh(Ru) \exp(-uR)}{uR} + \frac{\beta + u}{2r_3 R u^2} \begin{Bmatrix} g_1 \\ g_2 \end{Bmatrix} \right],$$

$$A^2 = -\frac{\mu \beta (\beta + \kappa)^2}{\pi (\beta + u)^2}, \quad (13)$$

$$g_1 = \frac{1 - \exp(-\beta r_3)}{\beta} + \beta \frac{\exp(-\beta r_3) - \exp(-ur_3)}{\beta^2 - u^2} - \frac{\sinh(ur_3) \exp(-2uR)}{\beta + u},$$

$$g_2 = \sinh(Ru) \left[\frac{\exp(uR)}{\beta - u} - \frac{\exp(-uR)}{\beta + u} \right] \exp(-ur_3) - \frac{2u^2}{\beta(\beta^2 - u^2)} \sinh(\beta R) \exp[\beta(R - r_3)];$$

$$\langle \nu | G(r', r'') | \nu \rangle = B \left[\frac{1}{\beta} - \frac{\exp(-2uR)}{\beta + u} + \frac{\beta + u}{r_3 u} \begin{Bmatrix} g_1 \\ g_2 \end{Bmatrix} \right],$$

$$B = \frac{\beta(\beta + \kappa)^2}{u(\beta + u)}, \quad (14)$$

$$g_1 = \frac{1 - \exp(-ur_3)}{\beta^2 - u^2} - u^2 \frac{1 - \exp(-\beta r_3)}{\beta^2(\beta^2 - u^2)} - \frac{\sinh(ur_3) \exp(-2uR)}{(\beta_u + u)^2},$$

$$g_2 = \left[\frac{\exp(uR)}{\beta - u} - \frac{\exp(-uR)}{\beta + u} \right]^2 \frac{\exp(-ur_3)}{2} + \frac{u^2}{\beta^2 - u^2} \left[\frac{1}{\beta^2} - \left(\frac{1}{\beta^2} + \frac{2}{\beta^2 - u^2} + \frac{r_3 - 2R}{\beta} \right) \times \exp(2\beta R) \right] \exp(-\beta r_3).$$

These relationships together with Eq. (11) completely determine the effective potential $U(r_3)$.

Let us investigate some features of this potential. As $r_3 \rightarrow 0$, Eq. (11) together with Eqs. (12)–(14) yield the simple relationship

$$1 = 2 \left(\frac{\beta + \kappa}{\beta + u} \right)^2 \quad (15)$$

for $u(0)$, which is independent of the electron-atom repulsion radius and determines the greatest possible value of the wave number of the effective potential:

$$u_{\text{max}} = (\sqrt{2} - 1)\beta + \sqrt{2}\kappa.$$

Interestingly, the effective potential vanishes only when there is virtual coupling in the electron-atom pair, i.e., at

$$\kappa_{\text{lim}} \approx -0.293\beta. \quad (16)$$

The depth of the potential remains constant as $\kappa \rightarrow 0$.

At the maximum possible values of r_3 , Eq. (11) simplifies and acquires the same form as in the zero-radius case.³ In particular, for $\kappa/\beta \ll 1$ the leading term in the solution of Eq. (11) can be written as follows:

$$u = c/r_3 + \kappa,$$

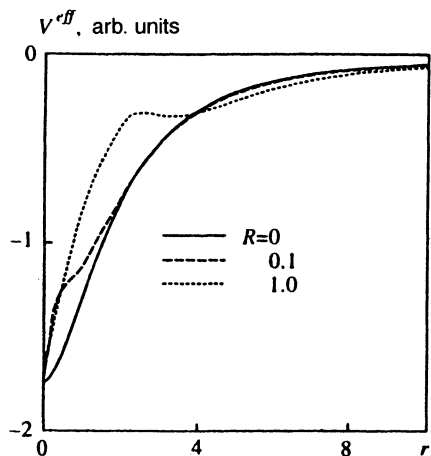


FIG. 1. Effective potentials for real pair coupling; $\kappa=0.1$. The necessary explanations are given in the text.

where the constant $c=0.5671\dots$ is the solution of the equation $c=\exp(-c)$. This determines the finite range in which the effective potential acts in the case of virtual coupling $\sim\kappa^{-1}$, or an infinite range in the case of real coupling. Here $u\rightarrow\kappa$ and, as noted in Ref. 3, we must call the quantity

$$V^{\text{eff}}=U(r_3)+\kappa^2/2\mu, \quad (17)$$

a quasi-two-particle potential for $\kappa>0$. The quantity is shifted by the binding energy of the pair. There is no need in such a procedure for virtual coupling, and we can as usual call U the effective potential. The above remark concerning the replacement of the reduced mass of the system consisting of two atoms and one electron, $m_{3,21}$, by the electron mass μ becomes obvious in this case. When μ is replaced by $m_{3,21}$, the asymptotic value of the potential is not the pair energy but a quantity shifted in relation to that energy by a constant $\sim\mu/M$.

Breaking up the effective potential V^{eff} into two terms,

$$V_1^{\text{eff}}=-\frac{(u-\kappa)^2}{2\mu}, \quad V_2^{\text{eff}}=-\frac{\kappa(u-\kappa)}{\mu},$$

we see that as in the case of a zero repulsion radius,³ the two potentials decrease differently in the region (1). For instance, the first term decreases according to a $1/r_3^2$ law and corresponds to the long-range Efimov behavior,¹ while the second term decreases only as $1/r_3$ and therefore,³ notwithstanding the factor κ , generates a finite spectrum even when $\kappa\rightarrow 0$. It is the second term that determines the spectrum of the system on the scales κ and β , which correspond to real systems. Here for r_0 in the region (1) we must take the greater of the two quantities β^{-1} and R .

Figures 1 and 2 depict the effective potentials calculated by Eq. (11) as functions of the distances between the atoms for different values of the repulsion radii for the real and the virtual electron-atom coupling, respectively. The values of the potentials are measured in arbitrary units, the same in both figures. The dimensional quantities r , R , and κ are made dimensionless by introducing the quantity β , i.e., $\beta=1$. The maximum differences between potentials with finite repulsion radii and the effective potentials with $R=0$

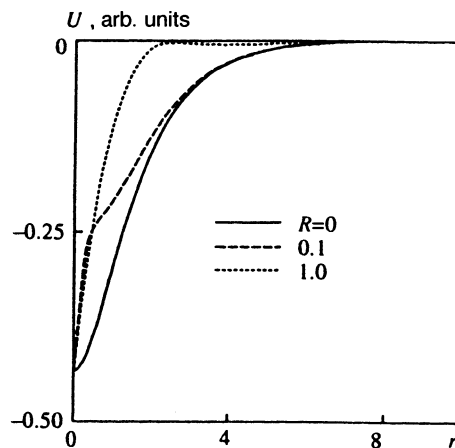


FIG. 2. Effective potentials for virtual pair coupling; $\kappa=0.1$. The necessary explanations are given in the text.

(see Ref. 3) are observed in the region where $r\sim 2R$ and consist in the following: in the region where r is slightly greater than $2R$ the decay of the potentials sharply diminishes, even leading to the appearance of a local minimum (see the curves with $R=1$), while for $r<2R$ the potentials with a finite repulsion radius decay much faster, “catching up” with the potentials without repulsion, since their value at zero does not depend on R .

Such behavior of the effective potential can be explained by a fairly simple interaction model. For large distances between the atoms the electron wave function can be represented by a sum of pair wave functions with each atom.⁷ Then the effective potential is defined as the potential energy averaged over the wave function. In the resonant case ($\kappa/\beta\ll 1$) the asymptotic expression for the pair wave functions contains a factor of the $1/r$ type. In the region (1), i.e., for $\kappa r_3\ll 1$, this yields terms of the $1/r_3^2$ and $1/r_3$ type. At smaller distances the pairwise wave functions become highly distorted. Here the electron density between the atoms begins to decrease because of the zero boundary condition at the two spheres with an area of $8\pi R^2$, which leads to a weakening of attraction. As the repulsion area decreases for $r_3<2R$, the potential again begins to deepen, reaching its limit when the atoms merge. This situation corresponds to a wave function with a doubled attraction potential. The doubled Yamaguchi potential results in motion with a wave number defined by Eq. (15). Figure 2 clearly shows the higher rate of decay of the effective potential U . Such behavior can be explained by the sign of the term with a decay of the $1/r_3$ type, opposite to the sign of κ .

Concluding this section, we note that the large value of β corresponds to deep narrow potentials. Attraction in electron-atom systems is determined by a polarization potential of the $1/r^4$ type, which is shallower and wider. Hence for real systems of atomic physics, β differs little from κ , and the value of the dimensionless radius, βR , is much smaller than unity, which corresponds to curves with $R=0.1$.

TABLE I. Comparison of experimental and model cross sections of electron–helium elastic scattering.

Energy, eV	Scattering cross section, a_0	
	Experiment	Fit
1.0	19.9	19.90
5.0	17.4	17.40
10.0	13.8	13.90
15.0	11.3	10.97
20.0	9.34	8.542

5. THE BOUND STATES OF He_2^-

For the sake of an example we examine a system consisting of two helium atoms and an electron. The pairwise helium–helium potential is chosen in the form of a Morse potential whose parameters do not produce a bound state of a He_2 molecule:¹⁰

$$V_3 = 4V_0(y^2 - y), \quad y = \exp[-c(1 - r_3/\sigma)],$$

where the depth V_0 of the potential is 11.0 K, and the parameters c and σ determining the shape of the potential are 6.00 and 2.62 Å, respectively.

The electron–helium potential was taken in the form of (2). The parameters R , κ , and β of this potential were found by fitting the S -wave scattering cross section for such a potential with the experimental data via the least squares method. The scattering cross section can easily be found theoretically by allowing for (8). The experimental values in numerical form are taken from a review by de Heer.¹¹ The parameters of the potential (2) obtained in this manner were $\kappa/\beta = -0.225$, $\beta = 0.967 \text{ \AA}^{-1}$, and $R = 0.693 \text{ \AA}$ and yield satisfactory agreement between the experimental and model values of the scattering cross section. The quality of the fitting process can easily be seen from Table I, where the energy is given in electron volts and the scattering cross section in units of the Bohr radius.

The rms value of the relative deviations of the model and experimental data of roughly 4% builds up at energies where the experimental cross sections are higher than the unitary limit in the S -wave.

After we have found the pair interaction, we can easily calculate the effective potential. As the values of the parameters show, there can be no bound electron–helium pair ($\kappa < 0$). More than that, the effective potential is at the threshold of appearance (16) and must be extremely shallow. Indeed, substituting the values of the parameters of the electron–helium potential into Eq. (11), allowing for Eqs. (12)–(14), and solving the implicit equation numerically, we obtain the maximum value for the effective potential at zero, $\approx 3.8 \text{ K}$, while the total potential $U_{\text{tot}} = V_3 + U$ change the depth only by 1.3 K, i.e., by 12%. However, this range is much larger than that of the helium–helium interaction potential. This becomes especially evident if one looks at Fig. 3, which depicts the total potential and the Morse potential for the helium–helium pair. We see that the effective potential has a volume no smaller than that of V_3 . To compare the characteristic volumes we use the quantity

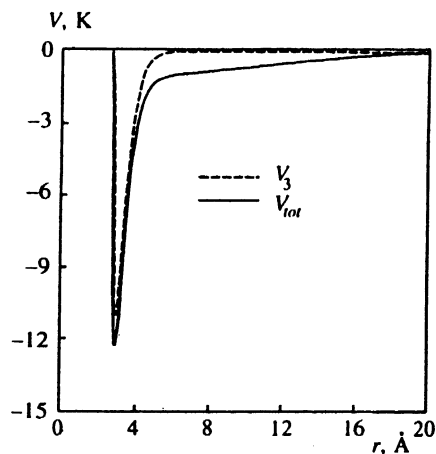


FIG. 3. The potentials V_3 and V_{tot} of the helium–helium interaction in the He_2 and He_2^- systems. The necessary explanations are given in the text.

$$J = \frac{2}{\pi} \int \sqrt{-MV} dr_3,$$

which enters into Calogero's estimate (see, e.g., Ref. 12) for the number of levels n_c . Here $n_c < J$. Integration is over the attraction region of the potential. A simple analytic calculation yields for the Morse potential the value $J_M \approx 0.835$, while a numerical calculation for the effective potential in the range of attraction of the total potential yields $J_{\text{eff}} \approx 2.27$. Here the total potential yields $J_{\text{tot}} \approx 2.73$. Thus, the exchange potential U is roughly 2.7 times as effective as the helium–helium potential V_3 .

The value of the quantities J can be used to estimate the number of levels generated by all potentials together and separately. In particular, the helium–helium potential does not produce any bound state, while the effective and total potentials can have no more than two bound states. Numerical calculations done by the semiclassical Bohr–Sommerfeld formula confirm the validity of such an estimate. The good agreement of the results of semiclassical calculations with those obtained by numerical solution of the Faddeev equations has been demonstrated earlier in Ref. 3. For calculations we used the quantization formula

$$\int_{r_{\text{min}}}^{r_{\text{max}}} \sqrt{M(E_n - V)} dr_3 = \pi(n + 0.5),$$

where integration is up to the turning points. Below is information about the spectrum generated by the effective potential. For its calculation the left boundary was determined from the turning point in the total potential. The Morse potential V_3 generates no bound states. The effective potential U generates a single bound state with a binding energy -0.487 K . The total potential generates two bound states with binding energies -0.813 K and $-3.5 \times 10^{-5} \text{ K}$.

6. CONCLUSION

The approach developed in this paper for describing three-particle systems with strong repulsion in pairwise potentials can be formulated not only for attraction in separable form but for potentials of an arbitrary type. The solution of

the spectral problem for determining the effective potential will in no way differ from approaches that use the expansion in the two-center basis and will require the same amount of effort. On the other hand, using a separable potential of the Yamaguchi type does not limit the approach. With another separable potential only the relationships (12)–(14) change. If we need to use separable potentials with a system of deep levels, we can use a multirank separable potential, which leads to complications in the expressions but does not change the principles of the approach. The solution of such problems is simpler because of the high percentage of analytic calculations in comparison to the two-center basis expansion.

The example of the He_2^- system with the weakest possible polarizability of the atoms and the lightest possible centers suggests that the spectrum contains an asymptotic part caused by long-range action in all diatomic negative ions. The author hopes soon to obtain results from calculations for specific systems such as diatomic negative ions and systems consisting of two heavy atoms and helium, whose mass ratios also suggest the presence of a long-range component in the three-particle spectrum.

I would like to thank N. Zh. Takibaev for his interest in my work.

¹⁾In this work we take Planck's constant to be $\hbar = 1$.

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