

Collision of Rydberg atom A^{**} with ground-state atom B. Optical potential

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The method of optical potential was used to calculate slow collision of Rydberg atom A^{**} with ground-state atom B. As an example, calculations were carried out for the $Na^{**}(nl) + He$ system.

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In spite of the progress in solving some problems of the physics of Rydberg atom collisions, one of the most important problem, namely, elastic scattering is still poorly understood, in contrast to the atomic scattering in the ground and low-lying excited states. The latter can be treated, in principle, using close-coupling approximation on the basis of the adiabatic potential energy curves. However, for the Rydberg collisions, the inelastic transitions are not localized and *adiabaticity* is broken. In this case, the three-particle approach seems to be most appropriate. This approach immediately leads to the effective energy-dependent two-particle optical potential. In this letter, the optical potential is derived for the elastic Rydberg atom collisions and a particular example of such potentials is given. In the standard theory, a non-local operator \mathbf{V}_{opt} is introduced, and the many-particle equation is constructed for its definition. This statement of the problem has the formal character, and it cannot be resolved without additional assumptions about the interacting system [1]. In this work, we consider slow elastic collision of a Rydberg atom A^{**} ($n \gg 1$) with ground-state atom B (n is the principal quantum number of the Rydberg level). We restrict ourselves to the case where the total energy of the system is $E < 0$ and calculate the optical potential for a structureless B particle. The optical potential of the $Na^{**}(nl) + He$ system is calculated as an illustration.

The total energy of the system is ($\hbar = e = m_e = 1$)

$$E = -1/2\nu_l^2 + E_k, \quad (1)$$

where $\nu_l = n - \mu_l$ is the effective principal quantum number, μ_l is the quantum defect, l is the electron angular momentum with respect to A^+ , and E_k is the initial collision energy. The interaction potential U_{A+B} of ion A^+

with atom B is assumed to be known. To solve the eigenvalue problem, we use the following integral equation for the level-shift operator τ [2]:

$$\tau = U_{A+B} \mathbf{G}(E) \tau. \quad (2)$$

The interaction operator of the three-particle system ($A^+ - B$) + free electron e^- is local and written as

$$\begin{aligned} U_{A+B}(\mathbf{R}, \mathbf{R}'; \rho, \rho') = \\ = (2\pi)^6 U_{A+B}(R) \delta(\mathbf{R} - \mathbf{R}') \delta(\rho - \rho'), \end{aligned} \quad (3)$$

where \mathbf{R} and ρ are the ion A^+ and electron coordinates measured from atom B. The Green's operator $\mathbf{G}(E)$ describes the $A^{**} + B$ system without interaction U_{A+B} and obeys the Dyson equation

$$\mathbf{G}(E) = \mathbf{G}_{A^{**}B}(E) + \mathbf{G}_{A^{**}B}(E) \mathbf{V}_{e-B} \mathbf{G}(E), \quad (4)$$

where \mathbf{V}_{e-B} is the operator of $e^- - B$ interaction, and the Green's operator $\mathbf{G}_{A^{**}B}(E)$ describes the noninteracting $A^{**} + B$ system with a given energy E .

The energy-dependent operator of nonlocal optical interaction is introduced in the theory as

$$\tau = \mathbf{V}_{opt}(E) \mathbf{G}_{A^{**}B}(E) \tau, \quad (5)$$

$$\mathbf{V}_{opt}(E) = U_{A+B} + U_{A+B} \mathbf{G}_{A^{**}B}(E) \mathbf{V}_{e-B} \mathbf{G}(E) \mathbf{V}_{opt}(E). \quad (6)$$

Using Eq.(4), the expression for the operator \mathbf{G} in Eq.(6) can be rewritten as [2]

$$\mathbf{G} = \mathbf{G}_{A^{**}B} + \mathbf{G}_{A^{**}B} \mathbf{T}_{e-B} \mathbf{G}_{A^{**}B},$$

where \mathbf{T}_{e-B} is the collision operator between the weakly bound electron and atom B. This representation is exact. It is convenient to use the Heitler-type equation

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and transfer to the real scattering matrix \mathbf{K}_{e-B} (which is constructed, as known, for standing waves)

$$\mathbf{T}_{e-B} = \mathbf{K}_{e-B} - i\mathbf{K}_{e-B}\mathbf{T}_{e-B}.$$

As a result, operator (6) takes the form

$$\mathbf{V}_{opt} = \mathbf{U}_{A+B} + \mathbf{U}_{A+B}\mathbf{G}_{A^{**}B} \times \\ \times [(\mathbf{1} + i\mathbf{K}_{e-B})^{-1}\mathbf{K}_{e-B}]\mathbf{G}_{A^{**}B}\mathbf{V}_{opt}. \quad (7)$$

It follows from Eq.(7) that the imaginary part of operator \mathbf{V}_{opt} appears due to the electron interaction with the perturbing atom B, leading to the virtual transitions accompanied by a change in its momentum and angular momentum. By definition, the function $\mathbf{G}_{A^{**}B}$ is a convolution

$$\mathbf{G}_{A^{**}B}(\mathbf{R}, \mathbf{R}'; E) = \\ = \frac{1}{(2\pi)^3} \int e^{i\kappa\mathbf{R}}\mathbf{G}_{A^{**}}(E - E_\kappa)e^{-i\kappa\mathbf{R}'} d\kappa, \quad (8)$$

$$E_\kappa = \kappa^2/2M_c,$$

where $\mathbf{G}_{A^{**}}$ is the Green's operator of the isolated Rydberg atom and M_c is the reduced mass of particles A^+ and B. Expanding Eq.(8) in terms of spherical harmonics, we have

$$\mathbf{G}_{A^{**}B}(E) = \frac{2}{\pi} Y_{\tilde{L}\tilde{M}}(\mathbf{R}/R) Y_{\tilde{L}\tilde{M}}^*(\mathbf{R}'/R') \times \\ \times \int_0^{\kappa_{max}} j_{\tilde{L}}(\kappa R) j_{\tilde{L}}(\kappa R') \mathbf{G}_{A^{**}}(E - E_\kappa) \kappa^2 d\kappa. \quad (9)$$

Here, \tilde{L} and \tilde{M} are the momentum and its projection on to the vector $\mathbf{R} - \mathbf{R}'$, respectively; $j_L(x)$ is the Bessel spherical function of the first kind of order L ; and $Y_{LM}(\theta, \varphi)$ is the spherical function. This expression is real, because, according to Eq.(1), the Green's function of Rydberg atom $\mathbf{G}_{A^{**}}$ is defined for negative energy and corresponds to the electron bound state in the entire region of electron coordinates and the coordinates of atom B. Since the main contribution to integral (9) comes from the classically allowed region, the maximum momentum is determined from the condition

$$0 \leq E + \frac{1}{R} - \frac{\kappa^2}{2M_c},$$

and is equal to

$$\kappa_{max} = \sqrt{2M_c(E + 1/R)}, \quad (10)$$

where $I_A^{-1} \leq R \leq 2\nu_l^2$, and I_A is the ionization potential of atom A.

The behavior of weakly bound electron near perturbing atom B, i.e. at $\rho, \rho' \ll R$, is of the greatest interest.

In this region, the following general representation takes place [2]

$$\mathbf{G}_{A^{**}}(\rho, \rho'; \mathbf{R}, \varepsilon) = \mathbf{G}_0^{(c)}(\rho, \rho'; \varepsilon) + 2 \sum_{s, s'} |s\rangle \langle s'| g_{ss'}(\mathbf{R}, \varepsilon). \quad (11)$$

The matrix elements are

$$g_{ss'}(\mathbf{R}, \varepsilon) = [p_e(\varepsilon) \cot \pi\nu(\varepsilon) \delta_{ss'} + \alpha_{LL'}^{II'}(\mathbf{R}, \varepsilon) \delta_{M0} \delta_{M'0}]. \quad (12)$$

Here, $p_e(\varepsilon) = [2(\varepsilon + 1/R)]^{1/2}$ is the electron quasiclassical momentum, $\nu(\varepsilon) = (-2\varepsilon)^{-1/2}$ is the effective principal quantum number; $|s\rangle$ is the electron wave function

$$|s\rangle = |lmLM\rangle = j_L(p_e\rho) Y_{lm}(\mathbf{R}/R) Y_{LM}(\theta, \varphi);$$

θ is the angle between the vectors $\mathbf{p}_e(\varepsilon)$ and ρ , L and M are the electron orbital momentum with respect to atom B and its projection onto the vector \mathbf{R} , respectively; and $\mathbf{G}_0^{(c)}$ is the smooth part of the Coulomb Green's function

$$\mathbf{G}_0^{(c)}(\rho, \rho'; \varepsilon) = -\frac{\cos(p_e|\rho - \rho'|)}{2\pi|\rho - \rho'|}.$$

The matrix $\alpha_{LL'}^{II'}(\mathbf{R}, \varepsilon)$ in Eq.(12) is defined as

$$\alpha_{LL'}^{II'}(\mathbf{R}, \varepsilon) = 2\pi^2 \sqrt{(2L+1)(2L'+1)} \times \\ \times \frac{(-1)^{l+l'+1} (\nu(\varepsilon))^3 \tan \pi\nu(\varepsilon) \tan \pi\mu_l}{\sin^2 \pi\nu(\varepsilon) \tan \pi\nu(\varepsilon) + \tan \pi\mu_l} \times \\ \times \tilde{\varphi}_{L\varepsilon}^{(l)}(R) \tilde{\varphi}_{L'\varepsilon}^{(l')}(R) |Y_{lm}(\mathbf{R}/R)|^2 \delta_{ll'}, \quad (13)$$

where the radial wave functions

$$\tilde{\varphi}_{L\varepsilon}^{(l)}(R) = \begin{cases} Q_{l\varepsilon}(R, \nu), & L = 2k \\ Q_{l\varepsilon}(R, \nu - 1/2), & L = 2k + 1 \end{cases} \\ (k = 0, 1, 2 \dots),$$

differ from each other by the phase shift of $\pi/2$ and are expressed in terms of the Whittaker functions

$$Q_{l\varepsilon}(r, \nu) = \frac{W_{\nu, l+1/2}(2r/\nu)}{r\nu\sqrt{\Gamma(\nu-l)\Gamma(\nu+l+1)}},$$

where $\Gamma(x)$ is the gamma function.

To find the explicit form of optical potential, let us introduce the basis wave functions of the $(A^+ + B) +$ free electron system in the following form

$$|q(\mathbf{R}, \rho)\rangle = \frac{1}{(2\pi)^3} \exp[i(\mathbf{k}\mathbf{R} + \mathbf{p}_e(\varepsilon)\rho)].$$

Let us use the first-order of perturbation theory and replace the operator \mathbf{V}_{opt} on the right-hand side of Eq.(6) by the local operator (3). Then the optical potential is defined as a matrix element

$$V_{opt} = \langle q | \mathbf{V}_{opt} | q \rangle. \quad (14)$$

Integrating over the interatomic coordinates and using the symmetry property of operator

$$\langle s | \mathbf{K}_{e-B} | s' \rangle = (\mathbf{K}_{e-B})_{ss'} \delta_{ss'},$$

one has

$$\begin{aligned} V_{opt}(E, k, l, \tilde{L}, R) &= U_{A+B}(R) + 2^{14} \pi^4 U_{A+B}^2(R) \times \\ &\times |Y_{\tilde{L}0}(\theta = 0)|^4 [(1 + i\mathbf{K}_{e-B})^{-1} \mathbf{K}_{e-B}]_{LL} \times \\ &\times \left\{ \int_0^{\kappa_{max}} \kappa^2 d\kappa \kappa'^2 d\kappa' j_{\tilde{L}}^2(\kappa R) j_{\tilde{L}}^2(\kappa' R) \times \right. \\ &\times \left. \sum_{mM} g_{ss}(R, \varepsilon_\kappa) g_{ss}^*(R, \varepsilon_{\kappa'}) |Y_{lm}(\mathbf{R}/R)|^2 |Y_{LM}(\boldsymbol{\rho}/\rho)|^2 \right\}, \end{aligned} \quad (15)$$

where $\varepsilon_\kappa = E - \kappa^2/2M_c$ and \tilde{L} is the initial orbital momentum of colliding particles A^{**} and B. The spherical function $Y_{lm}(\mathbf{R}/R)$ in Eqs.(13) and (15) should be replaced by $Y_{lm}(0)$. This is due to the fact that, under condition $l \ll \nu_i^{3/2}$, the electron motion near atom B is described by a plane wave with wave vector directed along the vector \mathbf{R} .

Under the conditions considered ($n \gg 1$), it is sufficient to restrict oneself to the case $L = 0$. The \mathbf{K}_{e-B} matrix can be replaced by the $\mathbf{K}_{e-B}^{(0)}$ matrix of free electron scattering with the energy $\varepsilon_e = E + 1/R - \kappa^2/2M_c$, because Rydberg electron behaves near atom B as a free particle [3]. Assuming for simplicity that atom B is a structureless particle, one can restrict oneself only by the first term in the long-wave length expansion of the $(\mathbf{K}_{e-B}^{(0)})_{ss}$ amplitude, i.e. by the $e^- - B$ scattering length a [4]. In this case, the Eq.(14) for given E_k takes the simple form

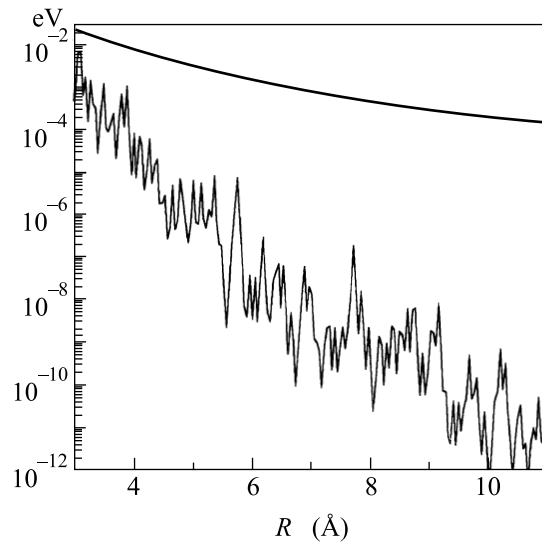
$$\begin{aligned} V_{opt} &= U_{A+B} + \Delta - i\Gamma/2, \\ \Delta(E, n, l, \tilde{L}, R) &= \frac{\pi a}{1 + a^2} S_{i\tilde{L}}(E, n, R), \\ \Gamma(E, n, l, \tilde{L}, R) &= \frac{2\pi a^2}{1 + a^2} S_{i\tilde{L}}(E, n, R), \end{aligned} \quad (16)$$

where the factor $S_{i\tilde{L}}(E, n, R)$ is equal to

$$\begin{aligned} S_{i\tilde{L}}(E, n, R) &= \\ &= \left[64\pi U_{A+B}(R) Y_{\tilde{L}0}^2(\theta = 0) Y_{i0}(\theta = 0) \times \right. \\ &\times \left. \int_0^{\kappa_{max}} j_{\tilde{L}}^2(\kappa R) g_{ss}(R, \varepsilon_\kappa) \kappa^2 d\kappa \right]^2. \end{aligned} \quad (17)$$

In accordance with Eq.(16), the real part of the shift is proportional to the scattering length a and depends on its sign. The width Γ is proportional to a^2 and is always positive. Note that the expression $S_{i\tilde{L}}(E, n, R)$

is an oscillating function of distance R and equals zero outside the classically allowed region of electron motion [i.e., at $R \geq (-E)^{-1}$]. It is easy to see that the shift and broadening of ionic potential are nonzero in the limit $k \rightarrow 0$. This result is physically understandable, because the weakly bound electron always may undergo virtual transition to the lower-energy state (with smaller principal quantum number).



The dependency of negative value of interaction potential $-U_{Na+He}$ (thick solid line) and Γ (thin solid line) on interatomic distance R calculated for $Na(10d) + He$ system. The calculations were carried out for $E_k = 2.72 \cdot 10^{-2}$ eV and $\tilde{L} = 0$

As an illustration, the dependencies of the potential U_{A+B} [5] and the width of the optical potential of the $Na(nl) + He$ system on the interatomic distance are given in Figure for $n = 10$, $\tilde{L} = 0$, and $l = 2$ at energy $E_k = 10^{-3}$, as calculated by Eqs.(16), (17) with $a = 1.15$ [6].

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