QUASIMOLECULAR TERMS FOR "AN INERT GAS ATOM – A RARE-EARTH ATOM" SYSTEM

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The results of calculations of the quasi-molecular terms (inter-atomic potentials) for: "an inert gas atom - a rare-earth atom" system are presented. The calculations are carried out with the use of the new effective pseudopotential method version and the exchange perturbation theory. The interaction of the 4f-electron shell of a rare-earth element with inert atoms and dependence of the interaction potential upon the electron angle moment projection of the corresponding quasi-molecule on the inter-nuclear axis is studied. Numeric results for: He-Tm and Ar-Tm systems are obtained.

While studying the adsorption spectra on the magnetic dipole transitions of rare-earth atoms in an inert medium it is important to know the cross-sections of the depolarization and non-adiabatic transitions under atomic collisions [1–5]. In this paper we present the results of calculations of the quasi-molecular terms (inter-atomic potentials) for "an inert atom (He, Ar) – a rare-earth atom (Tm)" system. The corresponding calculations are carried out with the use of a modified pseudopotential method and the exchange perturbation theory [2–4].

According to the standard method [1–4], in the first order of the exchange perturbation theory the energy of the system can be presented as:

$$\xi = (\Psi,\Psi)^{-1}\left(\Psi,\hat{H}\Psi\right), \qquad (1)$$

where $\hat{H}$ is the Hamiltonian, Ψ – the zeroth-order wave function:

$$\Psi = \left(N!/N_a!N_b!\right)^{1/2}\hat{A}\Psi_a\Psi_b\ . \qquad (2)$$

Here N is the total number of electrons; $N_a, N_в$ – the number of electrons of A atom and B atom, respectively; $\Psi_a, \Psi_в$ – atomic wave functions. Expression (1) can be rewritten as

$$\xi = \xi_a + \xi_в + U_n(R), \qquad (3)$$

where $\xi_a, \xi_в$ are the energies of isolated atoms; $U_n(R)$ is the potential of interaction (molecular term) of diatomic molecule and in the first order of the exchange perturbation theory it is defined as follows:

$$U_n(R) = (\Psi,\Psi)^{-1}\left(\Psi_a,\Psi_в,\hat{V}\sum_p(-1)^p P\Psi_a\Psi_в\right), (4)$$

Here $\hat{V}$ is the operator of interaction of atoms, P – the operator of substitution of electrons of the different atoms; $(-1)^p = +1$, if the substitution is even and –1 – if it is odd. Index n designs a set of quantum numbers of the isolated atoms, R – the inter-nuclear distance. The quantization axis is directed along the inter-nuclear axis. Below we use the wave functions of the atoms in the approximation of self-consistent field (our atomic numeric code is used [4, 6–8]). In this approximation it is possible to separate the wave function of the unoccupied 4f – shell Ψ_f in the full wave function Ψ_a [3]:

$$\Psi_a = \left(N_a!/N'!NN\right)^{1/2}\hat{A}_a\Psi'\Psi_f\ . \qquad (5)$$

Here Ψ' is the wave function of other electrons, N' – their number, $\hat{A}_a$ – an antisymmetrizer of all electrons for atom A. The algebraic structure of the interaction potential is as follows. The interaction operator can be rewritten in the following form:

$$\hat{V} = \hat{V}' + \hat{V}_f, \qquad (6)$$

where the part of interaction is dependent upon the coordinates of *f*-electrons $\hat{V}_f$.

$$U_n = \left(\Psi'\Psi_f\Psi_d, \hat{V}'\Psi'\Psi_f\Psi_d\right) + \left(\Psi'\Psi_f\Psi_d, \hat{V}_f\Psi'\Psi_f\Psi_d\right) -$$
$$-\left(\Psi'\Psi_f\Psi_d, \hat{V}'\sum_{kt} P_{kt}\Psi'\Psi_f\Psi_d\right) - \left(\Psi'\Psi_f\Psi_d, \hat{V}_f\sum_{kt} P_{kt}\Psi'\Psi_f\Psi_d\right) -$$
$$-\left(\Psi'\Psi_f\Psi_d, \hat{V}'\sum_{it} P_{it}\Psi'\Psi_f\Psi_d\right) - \left(\Psi'\Psi_f\Psi_d, \hat{V}_f\sum_{it} P_{it}\Psi'\Psi_f\Psi_d\right) \equiv$$
$$\equiv (\mathrm{I}) + (\mathrm{II}) + (\mathrm{III}) + (IV) + (V) + (VI), \quad (7)$$

Part (IV) is represented as:

$$(IV) = U_3(R) + U^{(2)}_{a\Omega}(R), \quad (8)$$

and for the potential $U^{(2)}_{a\Omega}(R)$ the following expression can be obtained:

$$U^{(2)}_{a\Omega}(R) \cong -N_3\sum_{x=2}^{2j} Q_{x0}\sum_{\lambda} s_{\lambda 0,00}\int \varphi_{\lambda 0}(r) \times$$
$$\times\left(\frac{1}{|R-r|^{x+1}} - \frac{1}{R^{x+1}}\right)\varphi_{00}(r)d^3r. \quad (9)$$

The integration in (9) is carried out beyond the boundaries of the region which is occupied by the 4f-shell (the region where the multi-pole moments Q_{x0} are formed). Here $\varphi_{00}(r)$ is the wave function of the 6*s* electron of the A atom, $\varphi_{\lambda 0}(r)$ – the wave function of the *ns*-(λ=0) and *np*-(λ=1) shells for the B atom ; N_s=2 – number of the valence electrons of A atom..

According to [3,4], the part of the interaction (dependent of the quantum numbers $a\Omega$) can be presented as follows:

$$\omega_{a\Omega} \equiv \sum_i U^{(i)}_{a\Omega}(R) = \sum_{x=2}^{2j} C^{j\Omega}_{j\Omega x0}U_x(a,R), \quad (10)$$

The full potential has the following form:

$$U_{a\Omega}(R) = U_0(R) + \omega_{a\Omega}(R), \quad (11)$$

where $U_0(R) = \sum_{i=1}^{4} U_i(R)$ is the "averaged" potential of interaction between atoms. For the potential $U^{(2)}_{a\Omega}(R)$ one can write:

$$U^{(2)}_{a\Omega}(R) = -(-1)^{j+S+L}(2j+1)^{1/2}C^{j\Omega}_{j\Omega 20}\begin{Bmatrix}2 & j & j\\ S & L & L\end{Bmatrix}U_2(L,R), \quad (11)$$

where the value $U_2(L,R)$ is determined as follows:

$$U_2(L,R) = 2\left(7/15\right)^{1/2} N_S < r^2 > \sum_{\lambda} s_{\lambda 0,00}\int \varphi_{\lambda 0}(r)\left(\frac{1}{|R-r|^3} - \frac{1}{R^3}\right)\varphi_{00}(r)d^3r, \quad (12)$$

We have carried out the calculations of the quasi-molecular terms (inter-atomic potentials) for "an inert atom (He or Ar) - a rare-earth atom (Tm)" system. We have used the wave functions for atoms, calculated on the basis of the *ab initio* model pseudopotential method and Dirac-Kohn-Sham method [4, 6–8]). The values of the $U_2(L,R)$ function for inter-nuclear distances $R \geq 6$ a.u.. (the typical values for atomic collisions at the particle energies ξ ~1000 K) are presented in Table 1.

Table.1. The relative potential of the interaction U_2 (L,R) of 4f–shell for Tm atom with atoms He and Ar.

R, a.u.	$U_2^{He}(L,R)$, a.u.	$U_2^{Ar}(L,R)$, a.u.	R, a.u.	$U_2^{He}(L,R)$, a.u.	$U_2^{Ar}(L,R)$, a.u.
6	$0{,}980 \cdot 10^{-4}$	$0{,}660 \cdot 10^{-3}$	11	$0{,}930 \cdot 10^{-7}$	$0{,}240 \cdot 10^{-5}$
7	$0{,}425 \cdot 10^{-4}$	$0{,}342 \cdot 10^{-3}$	12	$0{,}240 \cdot 10^{-7}$	$0{,}601 \cdot 10^{-6}$
8	$0{,}730 \cdot 10^{-5}$	$0{,}820 \cdot 10^{-4}$	13	$0{,}540 \cdot 10^{-8}$	$0{,}110 \cdot 10^{-6}$
9	$0{,}254 \cdot 10^{-5}$	$0{,}280 \cdot 10^{-4}$	14	$0{,}738 \cdot 10^{-9}$	$0{,}236 \cdot 10^{-7}$
10	$0{,}440 \cdot 10^{-6}$	$0{,}720 \cdot 10^{-5}$	16	$0{,}200 \cdot 10^{-9}$	$0{,}720 \cdot 10^{-8}$

References

1. I.G.Kaplan, O.V.Rodimova, *Usp. Fiz. Nauk* **126**, 103 (1978).
2. E.E.Nikitin, S.Ya.Umansky, *Nonadiabatic Transitions at Low Atomic Collisions* (Nauka, Moscow,1979).[in Russian].
3. D.V.Kupriyanov, I.M.Sokolov, *Chem. Phys.* **5**, 1165 (1986).
4. A.V.Glushkov, V.N.Polischuk *et al.*, *Opt. Spectr.* **84**, 501 (1998).
5. A.A.Radtzig ,B.M.Smirnov, *A Handbook on Atomic and Molecular Physics* (Energoatomizdat, Moscow, 1986).
6. E.P.Ivanova, L.N.Ivanov, A.V.Glushkov, A.E.Kramida, *Phys. Scripta* **32**, 512 (1985).
7. A.V.Glushkov, E.P.Ivanova, *J. Quant. Spectr. Rad. Transfer* **36**, 127 (1986).
8. A.V.Glushkov, L.N.Ivanov, *Phys. Lett. A* **170**, 33 (1992).

КВАЗІМОЛЕКУЛЯРНІ ТЕРМИ ДЛЯ СИСТЕМИ "АТОМ ІНЕРТНОГО ГАЗУ - РІДКОЗЕМЕЛЬНИЙ АТОМ"

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Представлено результати розрахунку квазімолекулярних термів (міжатомних потенціалів) для системи: "атом інертного газу – рідкоземельний атом". Розрахунки виконано на підставі нової ефективної версії методу псевдопотенціалу та обмінної теорії збурень. Досліджено взаємодію електроної 4*f*-оболонки рідкоземельного елементу з інертними атомами та залежність потенціалу взаємодії від проекції електронного кутового моменту відповідної квазімолекули на між'ядерну вісь. Чисельні результати отримано для систем: He-Tm і Ar-Tm.