

RYDBERG STATES OF DIATOMIC MOLECULES: *AB INITIO* PERTURBATION THEORY CALCULATION OF ALKALI DIMERS

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We have carried out the calculation of the potential curves for the ground and excited states, spectroscopic characteristics for the whole number of the diatomic alkali dimers A_2 ($A=Li, Na, K, Cs, Fr$) on the basis of the formally exact Rayleigh-Schrödinger perturbation theory with *ab initio* two-center approximation. The high-order contributions (due to polarization interaction between "above-core" valence quasi-electrons through polarizable core and mutual screening of "above-core" valence quasi-electrons) are accounted for effectively with the use of a new *ab initio* functionals. The are presented the calculated values of the spectroscopic constants (excitation energy T_e ; rotational and vibrational constants B_e, ω_e) for Rydberg states $n^1\Sigma_g^+$ ($n=4-6$) of Na_2 dimer are presented.

The calculation of spectroscopic characteristics for diatomic molecules is one of the urgent problems of modern molecular spectroscopy. It is related to the importance of these data for a number of applications, including laser spectroscopy, chemical physics, creation of the laser sources etc [1-15]. In this paper we study the potential curves for the ground and excited states, spectroscopic characteristics for the whole number of the diatomic alkali dimers A_2 ($A=Li, Na, K, Cs, Fr$). The corresponding calculation is carried out on the basis of the perturbation theory with *ab initio* two-center approximation [2]. We also present data on the spectroscopic constants (excitation energy T_e ; rotational and vibrational constants B_e, ω_e) for Rydberg states $n^1\Sigma_g^+$ ($n=4-6$) of Na_2 dimer.

Diatomic alkali molecules M_2 ($M=Li, Na, K, Rb, Cs$) can be treated as systems with two quasi-particles, moving in the field of the inert gases core $M^+ - M^+$. The ground state of the system is the state with two quasi-particles above the core, having the following form:

$$\Phi = \sum_{\xi\eta} C_{\xi\eta} \alpha_{\xi}^+ \alpha_{\eta}^+ \Phi_0,$$

where Φ_0 is the core state, C – a coefficient, taking into account angular symmetry. The electron Hamiltonian is as follows:

$$H = \sum_i \varepsilon_i \alpha_i^+ \alpha_i + \sum_{ij} F_{ij} \alpha_i^+ \alpha_j^+ + \sum_{ijkl} F_{ijkl} \alpha_i^+ \alpha_j^+ \alpha_k \alpha_l, \quad (1)$$

where ε_i are one-particle energies,

$$F_{ij} = - \sum_{\sigma=a,b} \int d^3r \varphi_i(r) V_M(r_{i\sigma}) \varphi_j(r),$$

$$F_{ijkl} = \iint r_1^3 dr_2^3 \varphi_i(r_1) \varphi_j(r_2) r_{12}^{-1} \varphi_k(r_2) \varphi_l(r_1).$$

Here $V_M(r_{i\sigma})$ is the core potential. It can be represented as

$$V_M = V_M(r_a, \theta_a, \varphi_a) + V_M(r_b, \theta_b, \varphi_b). \quad (2)$$

We use the basis, generated by the Hamiltonian of the quantum-mechanical problem for two centers of, as the zeroth order eigenfunction basis. The calculation of the considered system consisted of two parts: 1) the construction of the zeroth-order *ab initio* model approximation; 2) calculation of the different-order corrections for the perturbation theory with the effective account of the exchange-correlation effects and the effects of the higher-order perturbation theory.

We use here the *ab initio* procedure, proposed in [2] and based on the minimization of the gauge-dependent correlation contribution into the imaginary part of the electron energy of the molecule. The perturbation operator has the following form:

$$H_{\rho T} = \sum_{\delta} \sum_{ij} [r_{ij}^{-1} - V_M(r_{i\delta})], \quad (4)$$

where δ, i, j are the summation indices regarding the nuclei and electrons. In [2] the perturbation theory series for the secular operator matrix is build and the method of summation for this matrix diagrams is considered. The matrix element of the secular operator M has the following form:

$$M_{\xi\mu} = M_{\xi\eta}^{(0)} + M_{\xi\eta}^{(1)} + \dots + M_{\xi\eta}^{(i)},$$

where i is the full number of the quasi-particles, $M^{(0)}$ – the vacuum diagrams contribution (without end lines); $M^{(1)}$ – those for the one-particle diagrams (one pair of the end lines), $M^{(2)}$ – those for the two-quasi-particle diagrams (two pairs of the lines) etc. In the first-order perturbation theory it is necessary to calculate only the contribution of the two-quasi-particle diagrams which account for the inter-particle Coulomb interaction. This correction is equal to the energy of the inter-particle interaction $\Delta E^{(1)}$ and expressed through the matrix elements of conventional type over the zeroth-order wave functions. For the operator r_{12}^{-1} , as usually, the standard expansion over the Legendre polynomials of the first and second kind and spherical harmonics is used. In the theory of multielectron systems the correlation is usually taken into account by the superposition of the additional configurations, i.e. increasing of the secular matrix. These configurations can be divided into two groups: (1) the states with electron excitation from the core; their superposition takes into account the polarizational interaction with each other (they are described by the second-order polarization diagrams); (2) the states corresponding to the virtual excitation the external quasi-particles; the number of these quasi-

particles is not changed and the superposition of these states describes the effect of the mutual screening of particles by each other (the second-order screening diagrams). These two types of states give the correction of the second-order perturbation theory:

$$\Delta E^{(2)} = \Delta E_{pol}^{(2)} + \Delta E_{scr}^{(2)}.$$

The effective method for the account of both the first- and the second-type states without the increase of the secular matrix size is proposed in [2, 10]. It is based on the addition of the polarization operator which describes the polarization interaction of external quasi-particles through the polarizable core, into expression for the operator of the Coulomb inter-particle interaction. The account of the screening of the external quasi-particles can be carried out by means of the procedure, described in [10]. It enables one to take into account the screening type diagrams in all orders of the perturbation theory and improves the perturbation theory series convergence. The details of the numeric procedure are described in [2, 10, 12].

In Table 1 the results of calculation for the dissociation energies for a number of alkali dimers are presented. For comparison we give also the experimental data and results of other calculations: with different versions of the pseudopotential method (Gauss, Phillips-Kleyman, Gell-Mann potentials) and wave functions in the form of Gauss-, Heitler-London-type with Slater orbitals, natural orbitals, within the density-functional approach, in the multi-configuration approximation [3–15]. One can see a quite acceptable agreement between our numeric data and the available experimental results. The most principal moment of the present calculation is an accurate *ab initio* account of the effect of polarization interaction between the external quasi-particles through the polarizable core and effect of the mutual screening of these particles. Such procedure provides a reasonable agreement between the experiment and theory.

Table 1. The dissociation energies (eV) for RbM alkali dimers (M=Li, Na, K, Rb, Cs), calculated in the present paper, experimental data and results of calculations within other methods: a – experimental data; b – Gauss pseudopotential and model wave functions; c – the Gell-Mann pseudopotential and Gauss model wave function; d – the Gell-Mann pseudopotential and Heitler-London ansatz with Slater orbitals; e – Hartree-Fock potential + exact Phillips-Kleyman pseudopotential and Heitler-London ansatz with the Slater orbitals and account of the core polarization by means of effective potential; f – model pseudopotential and 13-configurational wave function; g – model potential and configurational interaction approximation with the use of approximate natural orbitals; H1- the present paper; H2 – perturbation theory with the zeroth approximation of the empirical model by Glushkov; k – semiempirical perturbation theory (with fitting D_e by experiment); l – local density approximation in the density-functional theory [1–15];

M(2)	a	b	c	d	e	f	g	H1	H2	k	l
RbLi								0.66	0.63		
NaNa	0.74	1.33	0.25	0.23	0.23		0.59	0.74	0.74	0.71	0.75
RbNa	0.58	0.58	0.58					0.58	0.57		
RbK	-							0.52	0.51		
Rb	0.49	0.49	0.02					0.48	0.46		
RbCs	-							0.45	0.42		

Table 2. Spectroscopic constants (T_e – the excitation energy, 100 cm^{-1} ; B_e, ω_e – rotational and vibrational constants, cm^{-1}) for the Rydberg states $n^1\Sigma_g^+$ ($n=4-6$) for Na_2 , calculated in the present paper and on the basis of other methods compared with the experimental data [12, 14]:

a – experimental data ; b – Hartree-Fock *ab initio* pseudopotential + core polarization];
 c – empirical pseudopotential + core polarization; d – the present paper [1-15]

		$4^1\Sigma_g^+$	$5^1\Sigma_g^+$	$6^1\Sigma_g^+$		$4^1\Sigma_g^+$	$5^1\Sigma_g^+$	$6^1\Sigma_g^+$		$4^1\Sigma_g^+$	$5^1\Sigma_g^+$	$6^1\Sigma_g^+$
A	T_e	283,3	317,7	325,6	B_e	0,0899	0,114	0,106	ω_e	108,7	109,4	123,7
B		285	319	327		0,0838	0,107	0,101		107	110	119
C		286	319	327		0,088	0,110	0,110		105	113	123
D		284	318	324		0,088	0,11	0,104		107	109	121

In Table 2 we present the results of calculation of the potential curves and spectroscopic constants for Rydberg states $n^1\Sigma_g^+(n=4-6)$ of the sodium dimer Na_2 . For comparison here we also present the experimental data and theoretical results, obtained on the basis of the calculations within the pseudopotential method, Hartree-Fock approach. As one can see from the table, there is a good agreement between the theory and experiment. In conclusion we point out that at present time the calculation of the Rydberg states is of great importance especially for laser spectroscopy, new laser sources creation, chemical physics, chemistry of plasma etc.

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РІДБЕРГІВСЬКІ СТАНИ ДВОХАТОМНИХ МОЛЕКУЛ: РОЗРАХУНОК ЛУЖНИХ ДИМЕРІВ НА ОСНОВІ ТЕОРІЇ ЗБУРЕНЬ З ПЕРШИХ ПРИНЦИПІВ

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Проведено розрахунки потенціальних кривих для основного та збуджених станів, спектроскопічних характеристик двоатомних лужних димерів A_2 ($A=Li, Na, K, Cs, Fr$) на основі формально точної теорії збурень Релея-Шредінгера з двоцентровим наближенням з перших принципів. Внески вищих порядків (завдяки поляризаційній взаємодії валентних квазіелектронів крізь здатний поляризуватися остов та взаємному екрануванню надостовних валентних квазіелектронів) ефективно враховано з використанням нових функціоналів з перших принципів. Проведено розрахунок спектроскопічних сталих (T_e – енергія збудження; B_e, ω_e – обертальна та коливна сталі) для рідбергових станів $n^1\Sigma_g^+$, $n=4-6$) димера натрію.