

CALCULATION OF ALKALI-METAL DIMERS ON THE BASIS OF A MODEL PERTURBATION THEORY

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On the basis of pseudopotential theory, within the framework of a formally accurate model perturbation theory of Rayleigh–Schrödinger type with a zero-approximation inoculating potential, the calculation of some diatomic alkali molecules in homo- and heteronuclear variants LiM ($M = Li, Na, K, Rb, Cs, Fr$) is considered. A local model potential of Gell-Mann type is adopted as the zero-approximation potential. The calculation results for the energy parameters – in particular, the energy of dissociation – are given; some of these results are obtained here for the first time. The calculation demonstrates the fundamental role of two basic second-order perturbation-theory effects in achieving acceptable accuracy: polarizational interaction of the valence particles through the core; and mutual screening of these particles.

INTRODUCTION

Calculation of the spectroscopic parameters of diatomic molecules is still a very important problem, since these parameters are important for a number of optical applications. Semiempirical and nonempirical pseudopotential (PP) theories are widely used in modern calculations of the parameters of diatomic molecules; this is mainly due to the effectiveness and simplicity of taking the influence of internal-shell electrons into account in the explicit description of the molecular system in the valence approximation; see [1-11], for example. Usually, two such theories are employed. The first is the model-PP method, based on semiempirical model PP that simulate the PP approximation of the frozen core; the parameters of the model PP are chosen so as to match the experimental data. These PP are intensively used in calculations of the parameters of diatomic molecules, because of their relatively simple mathematical form and the acceptable accuracy in calculating the energy properties – for example, the Rydberg-level energies for a number of molecules. At the same time, the use of this method in the absence of reliable experimental data for the molecules is problematic; this severely restricts its application. The use of the second type of PP theory, in which the valence orbitals are not required to be orthogonal to a specified set of core orbitals, essentially reduces to purely theoretical transformation of the initial equations for the valence electrons, i.e., to transformation to the frozen-core approximation. This means that the formal PP equations take no account of the most important correlation effects of the type of core polarization and energy dependence of the particle interaction. A promising approach is to take account of exchange-polarization effects in density-functional theory, using single-particles exchange-polarizational PP. In [12-14], exchange and correlation effects were taken into account by adding potentials that depend on the dipole α_d and quadrupole α_q polarizability of the core to the model PP. The deficiencies of this method include the need for preliminary determination of α_d and α_q (the accuracy of their calculation is low, as a rule) and the incomplete incorporation of the most important exchange-correlation effects. Experience in using model PP in molecular calculations nevertheless shows that these methods are sometimes able to reproduce the results of correct *ab initio* complete multielectron calculations with adequate accuracy – in particular, if molecules containing atoms from the first two periods of the Periodic Table and transition metals are considered [4-11]. Comparison of the results of PP calculations with the best calculations by the configurational-interaction method show that PP calculations give, on average, an error of ~10% or more in calculating electron-correlation effects. Evidently, PP

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TABLE 1. Parameters of Model Potential V_M (at. units) and Experimental Ionization Energy E of Alkali Atoms (eV)

Atom	A	κ	$-E$
Li	1,287	0,422	5,39
Na	1,826	0,536	5,14
K	1,989	0,449	4,32
Rb	1,640	0,358	4,18
Cs	1,672	0,333	3,88

methods are most appropriate for single-quasiparticle (i.e., with one electron above a core of filled electron shells) molecular alkali ions of type M_2^+ ($M = \text{Li, Na, K, Rb, Cs}$) [5, 8]. If there are several external electrons (quasiparticles) in the system, it is very important to take accurate account of the interelectron correlations and, unless correct methods are used, solution by PP methods may give results of poor accuracy; for more details, see [3, 4, 15]. In our view, the construction of model PP within the framework of Rayleigh–Schrödinger perturbation theory (PT), taking account of exchange-correlation effects as higher-order effects and with zero-approximation inoculating PP, is very effective and systematic. At least, this approach has been successfully implemented in calculations of atoms, ions, and molecules [13-30].

In the present work, on the basis of PP methods, within the framework of model PT, we consider the calculation of homo- and heteronuclear alkali diatomic molecules LiM ($M = \text{Li, Na, K, Rb, Cs, Fr}$), which are currently of great interest in numerous applications, including plasma chemistry [2, 5]. The model Hamiltonian of the system is constructed within the framework of Rayleigh–Schrödinger PT, with a zero-approximation inoculating PP [13-17]. A local model potential of Gell-Mann type is used as the zero-approximation PP [2]. Two main second-order PT effects play a fundamental role in ensuring acceptable accuracy: the polarizational interaction of the valence particles through the core; and their mutual screening. In the present work, novel procedures for taking these effects into account are adopted. It is shown that using empirical information on simpler corresponding ions in zero-approximation PT with PP in alkali-molecule calculations permits increase in accuracy of the result, without additional computational complexity.

2. PT CALCULATION METHOD. ZERO APPROXIMATION

In the PP approach, the calculation of molecules of type M_2 ($M = \text{Li, Na, K, Rb, Cs}$) may be reduced to calculating a system consisting of two external electrons (quasiparticles) moving in the field of ions of inert-gas atom type $M^+ - M^+$, which form the core [13-15]. The ground state of the system – a state with two quasiparticles above the core, in the secondary-quantization representation – takes the form

$$\Phi = \sum_{\xi\eta} c_{\xi\eta} a_{\xi}^+ a_{\eta}^+ \Phi_0,$$

where a^+ is the creation operator for the particles above the core; Φ_0 is the state of the core; the coefficient c takes account of angular symmetry. The electron Hamiltonian of the system takes the form

$$H = \sum_i \varepsilon_i a_i^+ a_i + \sum_{ij} F_{ij} a_i^+ a_j^+ + \sum_{ijkl} F_{ijkl} a_i^+ a_j^+ a_k a_l,$$

where ε_i are the single-quasiparticle energies, and

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

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

TABLE 2. Values of Parameters α , β , n , θ , and N (at. units), Equilibrium Distance R_e (at. units), and Ionic Dissociation Energy D_e (eV)

Ion	α	β	n	D_e	R_e	N	θ
Li_2^+	0,6111	0	3	0,95	6,36	0,3012	0,7239
LiNa_2^+	0,5996	0,0570	3		6,58	0,2147	0,7281
LiK_2^+	0,5722	0,0584	3		6,90	0,1166	0,7403
LiRb_2^+	0,5548	0,0603	3		7,21	0,1107	0,7523
LiCs_2^+	0,5364	0,0672	3		7,99	0,1038	0,7641
LiFr_2^+	0,5192	0,0743	3		8,14	0,0953	0,7792

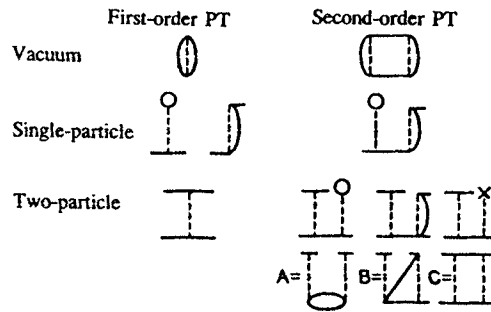


Fig. 1

Here $V_M(r_{i\sigma})$ is the single-particle model PP simulating the core potential in which the quasiparticles move. The interaction energy E_0 of the ions core M^* is defined as

$$E_0 = Z_a^c Z_b^c / R,$$

where R is the internuclear distance; Z_a^c , Z_b^c are the effective charges [31-35]. The procedure for correct determination of Z^c may be found in [31], for example. The model potential V_M chosen is a local potential of Gell-Mann type [5, 8]

$$V_M = -\frac{1}{r} + \frac{A}{r} e^{-2\kappa r}, \quad (1)$$

where the parameters A , κ of the potential are usually calibrated from the experimental ground-state energy of the alkali atoms (Table 1). The correct molecular model PP is expressed as a sum

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

In the systematic implementation of the PT method with zero-approximation PP, the eigenfunctions of the well-known quantum-mechanics problem of two centers with potential V_M must be used as the zero-approximation functions [35]. We consider this approach for the Li_2 molecule as our first illustration in the present work. The solution of the bicentric problem was considered in [13, 18, 33]. As our second illustration, we consider the Rayleigh-Ritz variational principle, with a trial wave function of the form [8]

$$\Psi(\lambda, \mu) = (R\lambda)^\mu e^{-(\alpha R\lambda + \beta R\mu)}, \quad (3)$$

where λ , μ are the usual elliptical coordinates: $\lambda = (r_a + r_b)/R$, $1 \leq \lambda \leq \infty$; $\mu = (r_a - r_b)/R$, $1 \leq \mu \leq 1$; α , β are variational parameters determined by minimizing the ground-state energy; n is an integer chosen so as to obtain the best energy; for more details, see [8]. Our third illustration is practically the same as the second, except that the parameters α , β , n are

chosen so as to reproduce the experimental dissociation energy of the corresponding ion M_2^+ . Calculation of the M_2 system thus breaks down into two stages: 1) construction of the zero-order model approximation, with determination of the PP parameters on the basis of empirical information; 2) calculation of corrections of various PT orders using a PT of Rayleigh–Schrödinger type, taking effective account of exchange-correlation effects as higher-order PT effects on the basis of the corresponding single-particle and multiparticle PP. The perturbation operator employed takes the form

$$H_{PT} = \sum_{\sigma} \sum_{ij} [r_{ij}^{-1} - V_{\alpha}(r_{i\sigma})], \quad (4)$$

where the subscripts σ , i , j correspond to summation over the nuclei and electrons, respectively.

3. CALCULATION METHOD. HIGHER-ORDER PT CORRECTIONS

In [13, 18], a series of PT for matrices of the secular operator were constructed, and methods of diagram summation for the secular-operator matrix were considered. The terms of such series were expressed as contributions to Feynmann diagrams, which were classified in terms of the number of end lines. In this classification, the matrix element M of the secular operator may be represented as

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

where i is the total number of quasiparticles; $M^{(0)}$ is the contribution of the vacuum diagrams (without end lines); $M^{(1)}$ is the contribution of single-quasiparticle diagrams (with one pair of end lines); $M^{(2)}$ is the contribution of two-quasiparticle diagrams (with two pairs of end lines); and so on. The contribution $M^{(0)}$ defines the core energy, while $M^{(1)}$ is the sum of single-quasiparticle states ξ_i . In the first order of PT, only the contribution of first-order two-quasiparticle diagrams, taking account of the direct Coulomb interaction of the quasiparticles, need be taken into account. The first-order correction is equal to the quasiparticle interaction energy $\Delta E^{(1)}$ and is expressed in terms of matrix elements of the usual type based on zero-approximation wave functions. For the operator r_{12}^{-1} , as usual, we employ the Neumann expansion in terms of secondary Legendre polynomials of the first and second kind and spherical harmonics; for more details, see [35]. Note that, in the first PT order, there are no two-particle diagrams with a compensating term $-V_M$ in H_{PT} . In the second PT order, however, such diagrams appear, but their contribution is significantly compensated by that of diagrams with intrinsically energetic insets, as shown by Tolmachev [22-25]. In what follows, we consider the second-order diagrams A, B, C (Fig. 1), for which the calculation must be conducted. In the theory of multielectron systems, the correlation is usually taken into account by the superposition of additional configurations, i.e., by expansion of the secular matrix. The additional configurations may be divided into two groups: 1) states with the excitation of core electrons: a state with one vacancy in the core and three electrons above the core; the superposition of these states taken account of the mutual polarizational interaction of the quasiparticles through the polarizable core (second-order diagrams A and B in Fig. 1); 2) states corresponding to the excitation of one of the external quasiparticles, with no change in the number of external particles; the superposition of these states describes external mutual screening of the external particles (second-order diagram C in Fig. 1). These two types of states result in a second-order PT correction

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

Note that this additive division is only possible in second-order PT; terms describing the interference of these effects appear in higher orders. The superposition of states of the second type would involve the calculation of very cumbersome matrix elements. States of the second type may be taken into account in the secular matrix, in principle, by means of the expression for $\Delta E^{(1)}$ for the matrix element. Here, however, a whole continuum of higher states must be taken into account in order to obtain the desired accuracy. An effective method of taking states of both the first and second types into account without increasing the size of the secular matrix (and additional computational complexity) was proposed in [26-29]; see also [15-19]; in this approach, a polarizational operator describing the interaction of external particles through the polarizational core is added to the Coulomb particle-interaction operator. The matrix elements of the polarizational operator, of the form [26, 13]

$$F_{\text{pol}}(\mathbf{r}_1, \mathbf{r}_2) = X \{ \int d^3 r \rho_c^{1/3}(\mathbf{r}) / |\mathbf{r}_1 - \mathbf{r}| \cdot |\mathbf{r} - \mathbf{r}_2| - \int \int d^3 r \rho_c^{1/3}(\mathbf{r}) / |\mathbf{r}_1 - \mathbf{r}| \cdot \int d^3 r \rho_c^{1/3}(\mathbf{r}) / |\mathbf{r} - \mathbf{r}_2| \} \int d^3 r \rho_c^{1/3}(\mathbf{r}), \quad (5)$$

TABLE 3. Dissociation Energy (eV) of Alkali Dimers LiM (M = Li, Na, K, Rb, Cs, Fr) Calculated by PT Method and in Other Approximations and Experimental Data

M	a	b	c	d	e	f	g	h1	h2	h3	κ	l
LiLi	1,05	1,57			0,24	0,89		0,93	0,92	0,97	1,03	0,98
NaLi	0,87	1,33	0,35	0,27				0,86	0,81			
KLi	0,75							0,76	0,70			
RbLi								0,66	0,62			
CsLi								0,58	0,52			
FrLi								0,53	0,45			

Note. a) Experimental data; b) Gaussian PP and model wave functions; c) Gell-Mann potential and Gaussian model wave functions; d) Gell-Mann potential and Gaitler–London sum with Slater orbitals; e) Hartree–Fock potential + precise Phillips–Clayman PP and Gaitler–London sum with Slater orbitals (taking account of core polarization in the form of an effective potential); f) model PP and 13-configuration wave function; g) model PP and configurational-interaction approximation, using approximate natural orbitals; h1-h3) present work, cases 1-3 (see text); κ) semiempirical PT (with experimental fitting of D_e); l) local-density approximation in the density-functional theory.

are the contributions due to the polarizational diagrams (Fig. 1). Here X is a numerical coefficient, determined by the procedure in [26]; ρ_c is the electron density of the core, disregarding the external quasiparticles. In calculating the polarizational correction, $\rho_c = \rho_a + \rho_b$ is assumed, and then $\rho_{a,b}$ are determined by the expressions in [13]. The general calculation procedure for $\Delta E_{\text{pol}}^{(2)}$ was described in [26]; see also [27]. Note that the angular components of the matrix elements r_{12}^{-1} and $F_{\text{pol}}(r_1, r_2)$ agree; therefore, taking the correction $\Delta E_{\text{pol}}^{(2)}$ into account reduces to modification of the radial integrals in the expression for $\Delta E^{(1)}$. Introducing F_{pol} allows the calculation to be reduced to a two-particle problem with an interaction potential $[r_{12}^{-1} + F_{\text{pol}}(r_1, r_2)]$, to the accuracy of second-order TP. The mutual screening of the external particles may be taken into account by adding the supplementary screening potential W_{scr} arising on account of the second external particle to the interaction potential of the external electron with all the core electrons in the zero-approximation Hamiltonian. The potential W_{scr} is chosen so that

$$\langle | \sum_{\gamma} \frac{\theta}{r_{1\gamma}} | \rangle = \langle | r_{12}^{-1} | \rangle,$$

where θ is the potential parameter (see below). The matrix elements here are calculated on the basis of the zero-approximation wave functions with an inoculating model potential. Other ways of taking screening effects into account are possible [27-33]. Including W in zero order allows ladder-type diagrams to be effectively taken into account in all PT orders (Fig. 1).

4. CALCULATION RESULTS

We now consider the calculation results given by the Rayleigh–Schrödinger PT method, with a zero-approximation inoculating model potential, for the dissociation energy D_e and the equilibrium distances R_e of a series of diatomic alkali-metal dimers: LiM (M = Li, Na, K, Rb, Cs, Fr). Table 1 gives values of A and κ in Eq. (1), as calibrated on the basis of empirical ground-state energies for alkali atoms [1, 13]. Table 2 gives values of the parameters α , β , n, N (N is the normalization constant) for the zero-approximation wave function found variationally for the corresponding molecular ions M_2^+ (by minimization). Of course, in the homonuclear case, $\beta = c$; in the heteronuclear case, $\beta \neq 0$. Table 2 also gives the parameter θ of the screening potential W_{scr} . Table 3 summarizes the results of calculating the dissociation energy for a lithium dimer in three cases: 1) the zero approximation is determined by solving the quantum-mechanics problem of two centers; 2) the zero-approximation wave function is a trial function with variationally defined parameters (Table 2); 3) the zero-approximation wave

function is a trial function with a parameter α chosen so as to match the experimental dissociation energy of Li_2^+ . The exchange-correlation effects in all cases are taken into account in the same way, by the method already described. Table 3 also gives the results for the dissociation energy of other diatomic alkaline molecules in case 2. For comparison, Table 3 includes literature data on the energy of some of the molecules obtained by other methods: various versions of the PP approach – in particular, with PP of Gauss, Phillips–Clayman, and Gell-Mann type and with wave functions of Gaussian and multiconfigurational type or in the form of a Gaitler–London sum with Slater orbitals and approximate natural integrals, and by the density-functional method in the multiconfigurational approximation [1-11, 13, 35]. Note the good agreement of our calculation results with empirical data. For a number of molecules, the energy values are obtained here for the first time. The most important aspect of the calculation is that the polarizational interaction of the external quasiparticles through the core and the mutual screening of these particles are accurately taken into account, in the PT framework. As a result, the accuracy of the results exceeds that of previous calculations. Analysis of the calculation of the lithium dimer in the three cases considered shows that the use of eigenfunctions of the bicentric problem as wave functions in the first approximation leads to more accurate results than does the use of molecular wave functions with the variational parameters α and β . Fitting the parameter α in the third case to the experimental dissociation energy of Li_2^+ leads to more accurate determination of D_e for Li_2 than does variational determination of α . This is obviously associated with the use of empirical information on a simpler related system when formulating the PT zero approximation in the theory of atomic and ionic calculation within an analogous approach [26-30]. In terms of diagrams, this means that the corresponding correlation diagrams are more completely taken into account. Note, in conclusion, that the calculation scheme in the present approach permits the use of the *ab initio* PP in the PT zero approximation, as was done for atomic systems in [28-30]. This implies that diatomic systems for which absolutely no experimental spectral or structural data exist can be calculated by our method. This topic will be considered in a separate work, along with a new selection principle for the PT basis with an inoculating zero-approximation PP; this selection principle is based on the Gell-Mann–Low adiabatic formalism [28] and is of enormous interest for relativistic quantum chemistry.

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