

CALCULATION OF ALKALINE METAL DIMERS IN TERMS OF MODEL PERTURBATION THEORY

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The problem of calculating diatomic alkaline metal (homo- and heteronuclear) molecules KM ($M = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) is treated in terms of a pseudopotential approach in the framework of a formally exact model perturbation theory of Rayleigh–Schrödinger type with a test zero-order potential. A Gell–Mann type local model potential is used as a zero-order potential. The results of calculations of energy parameters, in particular, dissociation energies, are given; some of them were obtained for the first time. The calculation demonstrated that two major effects of second-order perturbation theory: polarizing interaction of valence particles across the core and mutual screening of particles must be taken into account to achieve an acceptable accuracy of calculations.

INTRODUCTION

Calculating the energy characteristics of diatomic molecules is still an important problem, because this information is essential for physicochemical applications [1-15]. Modern calculations of molecules widely use semiempirical and nonempirical pseudopotential (PP) theories, primarily due to the efficient and simple procedure allowing for the innermost shell effect when explicitly describing a system in a valence approximation (see, e.g., [1-12]).

Theories of two types are generally employed. The first (model PP) type uses a semiempirical model PP (imitating PP in a frozen core approximation) with parameters chosen such that experimental data should be reproduced. These PP were actively employed in calculations of the parameters of diatomic molecules owing to their simple mathematical form and an acceptable accuracy of calculations of the energy properties such as the energies of Rydberg levels for a series of molecules, etc. At the same time, application of this effective method is problematic when reliable experimental data are lacking. The second type of PP theories are characterized by the absence of the requirement that the valence orbitals be orthogonal to a given set of core orbitals, and using these theories is reduced to essentially theoretical transformation of initial equations for valence electrons, i.e., actually to a change to a frozen core approximation. This means that the formal PP equations do not include the most important correlation effects such as core polarization and the energy dependence of particle interactions. It also seems promising to take into account exchange polarization effects in terms of density functional theory using one-particle exchange polarization PP.

In several papers [12-14], exchange and correlation effects were included by complementing the model PP with potentials depending on the dipole α_d and quadrupole α_q polarizability of the core. A disadvantage of this method is the necessity of previously finding α_d , α_q (the accuracy of this calculation is generally low) and incomplete inclusion of the most important exchange correlation effects. Nevertheless, the wide experience in using model PP in molecular calculations demonstrated that these methods are occasionally accurate enough to reproduce the results of correct *ab initio* full many-electron calculations, in particular, the calculations for molecules containing atoms of the first two periods of the periodical table and transition metals [4-11]. A comparison between the results of the PP and best configuration interaction calculations shows that the average error of calculation of electron correlation effects using PP is ~10% or more.

One-quasiparticle (with one electron above the core of filled electron shells) molecular alkaline ions M_2^+ , $M = \text{Li, Na, K, Rb, Cs}$ [5, 8] seem to be the most suitable objects for application of PP methods. In case of several outer electrons (quasiparticles) in a system, the problem of accurately calculating electron correlation effects becomes very important, and the PP technique gives low accuracy of calculations without using correct methods for solving this problem (for details, see [3, 4, 15]).

We believe that a very efficient and consistent procedure is constructing model PP in terms of Rayleigh–Schrödinger perturbation theory (PT) including exchange correlation effects as higher-order effects and using a test zero-order PP. This was at least realized in the theory of calculations of atoms, ions, and molecules [13-30].

Here we deal with the problem of calculating diatomic alkaline metal (homo- and heteronuclear) molecules KM ($M = \text{Li, Na, K, Rb, Cs}$) by the PP method in terms of model PT. This problem is currently of great interest since data about these molecules are relevant for some applications, including plasma chemistry, etc. [2, 5]. The model Hamiltonian of the system is constructed in terms of Rayleigh–Schrödinger type PT with a test zero-order PP [13-17]. A Gell–Mann type local model potential is used as zero-order PP [2].

Two major effects of second-order PT: polarizing interaction of valence particles via the core and their mutual screening are important for achieving an acceptable accuracy of calculations. This paper uses original procedures for calculating these effects. It is shown that using empirical information about simple ions in calculations of the corresponding alkaline molecules in terms of zero-order PT with a zero-order PP increases the accuracy of calculations without making additional computational efforts.

1. CALCULATION PROCEDURE. ZERO-ORDER APPROXIMATION

In the framework of the PP approach, the problem on calculating molecules of M_2 type ($M = \text{Li, Na, K, Rb, Cs}$) may be reduced to a problem of calculating a system of two outer electrons (quasiparticles) moving in the field of ions of noble gas type atoms $M^+ - M^+$ forming a core [13, 15].

The ground state of the system, which is a state with two quasiparticles over the core, in a secondary quantization representation is

$$\Phi = \sum_{\xi\eta} C_{\xi\eta} a_{\xi}^{\dagger} a_{\eta}^{\dagger} \Phi_0,$$

where a^{\dagger} is the creation operator of a particle over the core; Φ_0 is the state of the core; C is the coefficient taking into account angular symmetry. The electronic Hamiltonian of the system is

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

where ε_i are one-quasiparticle energies:

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

$$F_{ijkl} = \int \int dr_1^3 dr_2^3 \varphi_i(r_1) \varphi_j(r_2) r_{12}^{-1} \varphi_k(r_2) \varphi_l(r_1).$$

Here $V_M(r_{i\sigma})$ is a one-particle model PP imitating the potential of the core in which the quasiparticles are moving. The interaction energy E_0 between the M^+ ions of the core 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 effective charges ([31-35]). The procedure for correct determination of Z^c is given, for example, in [31]. As a model potential V_M we took a Gell–Mann type local potential [5, 8]:

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

TABLE 1. Parameters of the Test Model Potential V_M (au) and Experimental Ionization Energies E of Alkaline Atoms (eV)

Atom	A	k	$-E$
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

where A, k are the parameters of the potential usually tested with respect to the experimental ground-state energies of alkaline atoms (Table 1). A correct molecular model PP is represented as a sum

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

A consistent PT method with zero-order PP must use the eigenfunctions of the known quantum mechanical two-center problem with the potential V_M as zero-order functions [35]. Below this is realized for the K_2 molecule as one of the calculation variants. Earlier, we dealt with the two-center problem (see [13] and also [18, 33]). The Rayleigh–Ritz variational principle is employed as the second variant of calculation. A test wave function is the function [8]

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

where λ, μ are the standard 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 the variational parameters determined by minimization of the ground state energy; n is an integer chosen such that the best energy is obtained (for details, see [8]).

The third variant of calculation virtually coincides with the second one, except that the parameters α, β, n are chosen such that the experimental dissociation energy of the corresponding M_2^+ ion is reproduced. Thus the M_2 system is calculated in two steps: 1) constructing a zero-order model using empirical data for determination of the PP parameters; 2) calculating various n th-order PT corrections with the aid of Rayleigh–Schrödinger type PT with effective allowance for exchange correlations effects as higher-order PT effects using the corresponding one- and many-particle PP. The perturbation operator is

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

where σ, i, j are the summation indices over the nuclei and electrons, respectively.

2. CALCULATION PROCEDURE. HIGHER-ORDER PT CORRECTIONS

A PT series for a secular operator matrix was constructed and methods of summing the diagrams for the matrix were considered in [13, 18]. The terms of the series were represented as contributions of Feynman diagrams, which were classified according to the number of terminal lines. In agreement with this classification, the matrix element M of the secular operator was 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 vacuum diagrams (without terminal lines); $M^{(1)}$ is the contribution of one-quasiparticle diagrams (one pair of terminal lines), $M^{(2)}$ is the contribution of two-quasiparticle diagrams (two pairs of terminal lines), etc. The contribution $M^{(0)}$ determines the energy of the core. The contribution $M^{(1)}$ equals the sum of one-quasiparticle states ε_i .

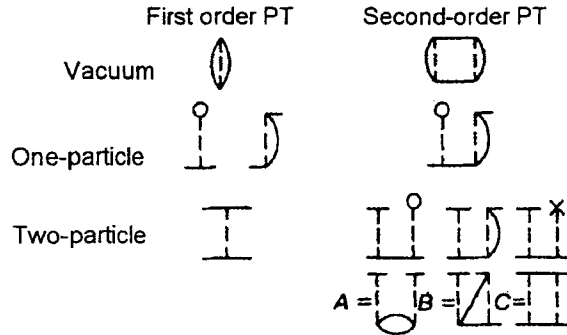


Fig. 1. Main Feynman diagrams of perturbation theory with a model zero-order potential. The diagram corresponding to V_M (vertex $\overset{\times}{\perp}$) is nearly completely compensated by the diagrams with Hartree–Fock insertions ($\overset{\circ}{\perp}$, $\overset{\circ}{\curvearrowright}$) in all orders of perturbation theory; A and B are the direct and exchange polarization diagrams, respectively, and C is a ladder-type diagram.

In first-order PT one should calculate only the contributions of two-quasiparticle first-order diagrams which take into account direct Coulomb interactions of quasiparticles. The desired first-order correction equals the interaction energy of the quasiparticles $\Delta E^{(1)}$ and is expressed in terms of the matrix elements of normal type on the zero-order wave functions. For the r_{12}^{-1} operator here, as usual, we employ Neumann's expansion into first- and second-order augmented Legendre polynomials and spherical harmonics (for details, see [35]). We note that the two-particle diagrams with a compensating term in $H_{PT}(VM)$ are absent in first-order PT but appear in second-order PT; however, as shown by Tolmachev, their contributions are largely compensated by the contributions of the diagrams with self-energy additions [22-25].

Below we consider second-order diagrams A , B , C (Fig. 1) for which the calculation must be fulfilled. In the theory of many-electron systems, correlation corrections are generally applied by adding configurations, i.e., by expanding the secular matrix. The additional configurations may be classified into two groups: 1) states with excitation of electrons from the core: states with one vacancy in the core and three electrons over the core; imposing these states means that polarizing interactions of quasiparticles with each other via the polarized core are taken into account (second-order diagrams A , B , Fig. 1); 2) states corresponding to excitation of one of the outer quasiparticles, the number of outer particles remaining the same; imposing these states defines the mutual screening effect of the outer particles (second-order diagram C , Fig. 1). These two types of state give a second-order PT correction:

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

We note that this additive classification is possible only in second-order PT; in higher orders, terms defining the interference of these effects will appear. Imposing the second-type states would lead to calculations of very cumbersome matrix elements. The second-type states may be taken into consideration in the secular matrix by expressing $\Delta E^{(1)}$ for the matrix element. However, it may be necessary to take into account the whole continuum of high-order states for achieving the desired accuracy.

An effective technique for calculating the first- and second-type states without expanding the secular matrix (and taking additional computational efforts) is suggested in [26-29] (also see [15-19]). This method involves addition of the polarization operator, defining the interactions of outer particles via the polarized core, to the Coulomb particle interaction operator.

The matrix elements of the polarization operator [26, 13]

$$\mathcal{P}_{\text{po}}(r_1, r_2) = X \left\{ \int d^3r \rho_c^{1/3}(r) / |r_1 - r| |r - r_2| - \left[\int d^3r \rho_c^{1/3}(r) / |r_1 - r| \int d^3r \rho_c^{1/3} / |r - r_2| \right] / \int d^3r \rho_c^{1/3}(r) \right\} \quad (5)$$

are diagram polarization contributions (Fig. 1). Here X is a numerical coefficient (its calculation procedure is described

in [26]); ρ_c is the electron density of the core neglecting outer quasiparticles. To calculate the polarization correction, for ρ_c we used an ansatz: $\rho_c = \rho_a + \rho_b$, and the densities $\rho_{a,b}$ were further defined in much the same way as done in [13]. The general calculation procedure for $\Delta E_{\text{pol}}^{(2)}$ is given in [26] (also see [27]).

We note that the angular parts of the matrix elements r_{12}^{-1} and $\mathcal{F}(r_1, r_2)$ coincide; therefore, applying the correction $\Delta E_{\text{pol}}^{(2)}$ amounts to modifying the radial integrals entering into the expression for $\Delta E^{(1)}$. Due to the introduction of \mathcal{F}_{pol} , the problem is reduced to the problem on two particles interacting via the potential $[r_{12}^{-1} + \mathcal{F}_{\text{pol}}(r_1, r_2)]$ to an accuracy of second-order PT. The mutual screening effect of outer particles may be included in the calculation by adding a screening potential W_{scr} (arising from the presence of the second particle) to the potential of interaction of the outer electron with all electrons of the core in the zero-order Hamiltonian. The desired potential W_{scr} is chosen such that

$$\langle |\sum_{\sigma} \theta / r_{i\sigma} | \rangle = \langle |r_{12}^{-1} | \rangle,$$

where θ is a potential parameter (see below). Here the matrix elements are calculated on the zero-order wave functions with a test model potential. There are alternative variants for calculating the screening effect [27-33]. Introduction of W into zero-order PT allows one to effectively calculate ladder-type diagrams in all orders of PT (Fig. 1).

3. RESULTS OF CALCULATION

Here we give the results of calculations of dissociation energies D_e of the equilibrium states R_e of some diatomic alkaline metal dimers KM (M = Li, Na, K, Rb, Cs) using the developed Rayleigh-Schrödinger type PT method with a test zero-order model potential. Table 1 gives parameters A, k of potential (1) tested with respect to the empirical energies of the ground state of alkaline atoms [1, 13].

Table 2 lists the test values of the parameters α, β, n, N (N is the normalization constant) of the zero-order wave function found by the variational method for the corresponding molecular ions M_2^+ (using the minimization procedure). Naturally, $\beta = 0$ in the homonuclear variant and $\beta \neq 0$ in the heteronuclear variant. Table 2 also lists the values of the θ parameter of the screening potential W_{scr} .

The results of dissociation energy calculations for the potassium dimer are given in Table 3 in three variants: 1) zero-order approximation is determined by solving the quantum mechanical two-center problem; 2) test function with variationally determined parameters is used as a zero-order wave function (Table 2); 3) test function with the α parameter chosen such that the experimental value of the dissociation energy of K_2^+ is reproduced is used as a zero-order wave function. In all variants, exchange correlation effects are taken into account as described above.

Table 3 also contains the calculated dissociation energies of other diatomic alkaline molecules. For comparison, Table 3 gives the available literature data for calculations by other methods, in particular, by different versions of the PP approach using Gaussian, Phillips-Kleiman, and Gell-Mann type PP and wave functions in Gaussian form, Heitler-London ansatz with Slater orbitals, multiconfigurational, approximated natural orbitals, density functional theory,

TABLE 2. Parameters $\alpha, \beta, n, \theta, N$ (N is the normalization constant), Equilibrium Distances R_e , and Dissociation Energies of Ions D_e (all values are given in atomic units, D_e in eV)

Ion	α	β	n	D_e	R_e	N	θ
KLi_2^+	0.5722	0.0584	3		6.90	0.1165	0.7403
KNa_2^+	0.5332	0.0473	3	0.73	7.30	0.1249	0.7648
K_2^+	0.4940	0	3	1.03	7.90	0.1444	0.7983
KRb_2^+	0.4836	0.0538	3	0.78	8.21	0.1216	0.8012
KCs_2^+	0.4784	0.0587	3	0.63	8.34	0.1163	0.8197
RFR_2^+	0.4693	0.0652	3		8.63	0.1112	0.8292

TABLE 3. Dissociation Energies (eV) of Alkaline Dimers KM (M = Li, Na, K, Rb, Cs, Fr) Calculated in This Work by the PT Method and Using Other Approximations and Available Experimental Data

M(2)	a	b	c	d	e	f	g	h1	h2	h3	k	l
LiK	1.05	1.57			0.24	0.89		0.77	0.71			
NaK	0.63	0.90	0.15					0.62	0.55	0.60		
K ₂	0.52	0.64	0.09	0.12	0.24		0.46	0.53	0.58	0.54	0.49	0.54
RbK								0.51	0.45	0.48		
CsK								0.47	0.41	0.44		
FrK								0.44	0.37			

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 Heitler–London ansatz with Slater orbitals; e) Hartree–Fock potential + exact Phillips–Kleiman PP and Heitler–London ansatz with Slater orbitals; core polarization correction is introduced as an effective potential; f) model PP and 13-configurational wave function; g) model PP and configuration interaction approximation using approximate natural orbitals; h) this work; 1, 2, 3 – variants of calculation (see text); k) semiempirical PT (with fitting of D_e to experiment); l) local density approximation in density functional theory.

and multiconfigurational approximation [1-11, 13, 35]. There is good agreement between the results of our calculations and the available empirical data. For several molecules, the energies were obtained for the first time.

The most important aspect of this calculation is an accurate inclusion of the polarization interaction of the outer quasiparticles via the core and mutual screening of the particles. Due to inclusion of these effects in the framework of PT, the results obtained here are more accurate than the data of previous calculations.

An analysis of the calculation of the dimer K_2 in the three versions shows that using the eigenfunctions of the two-center problem as wave functions in the zero-order approximation leads to more accurate results than using model wave functions with variational parameters α, β . Fitting the α parameter of the wave function to the experimental value of the dissociation energy of K_2^+ using the third version leads to a more exact value of D for K_2 than in the case of variational determination of α . This is probably explained by using empirical data on a simpler related system in zero-order PT, which is well known in the theory of calculations of atoms and ions in the framework of an analogous approach [26-30]. In terms of diagrams this means more complete allowance for the corresponding correlation diagrams.

In conclusion we emphasize that the calculation scheme of our approach provides for the possibility of using *ab initio* PP in zero-order PT, as done previously for atomic systems [28-30]. Due to this, our method may be applied to diatomic systems for which experimental spectral and structural data are lacking. This problem as well as the new principle of choosing a basis of PT with a test zero-order PP based on the Gell–Mann–Low adiabatic formalism [28] (which is of great interest for relativistic quantum chemistry) will be treated elsewhere.

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