A CONSISTENT APPROACH TO CONSTRUCTION OF THE MODEL VALENCE ELECTRON HAMILTONIAN:
M_2, M = Li, Na, K, Rb, Cs

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A consistent procedure is considered for the development of a correct model Hamiltonian for many-electron diatomic molecules in the framework of the Rayleigh–Schrödinger perturbation theory with zero approximation model potential and with corrections for the exchange-correlation effects as high order effects. Using the pseudopotential approach, we have calculated some molecular constants, in particular, the dissociation energy of homo- and heteronuclear diatomic alkaline molecules. It is shown that an accurate correction for the principal correlation effects (the polarization interaction of valence electrons via the polarized core and mutual screening of outer particles) is critical for obtaining a reasonable calculation accuracy. We suggest ways to improve the accuracy of calculations by using (in zero approximation of the perturbation theory) reliable empirical information about simple systems, such as the M_2^+ *ions (M = Li, Na, K, Rb, Cs).*

INTRODUCTION

Modern quantum-chemical calculations widely use the semiempirical and *ab initio* pseudopotential (PP) theories. These provide a simple and efficient method allowing for the influence of inner shell electrons of molecules when the latter are explicitly described in the valence approximation (for example, [1-11]). There are two types of PP theories. One of them (the PP model method) employs the semiempirical PP model simulating the frozen core approximation with parameters fitted to experimental data. Such PP were extensively applied to molecular calculations due to their simple mathematical form and an acceptable accuracy of calculation of some energies, e.g., the Rydberg energies, etc. At the same time, using this powerful method in the absence of reliable experimental data is problematic, which drastically restricts its applicability. The use of another type of PP, which does not require orthogonality of valence orbitals to a given set of core orbitals, is essentially reduced to purely theoretical transformations of the initial equations for valence electrons; this means in fact a transition to the frozen core approximation. Thus, formal PP equations neglect the most important correlation effects such as core polarization or the energy dependence of interparticle interactions. Still greater difficulties arise in obtaining the many-electron PP and deriving the PP equations for several valence electrons. A promising approach seems to be the inclusion of exchange polarization effects in the density functional theory using the one-particle exchange polarization PP. For many-particle effects the correct procedure has not been worked out. In some papers [12, 13] the exchange and correlation effects were included in the calculation by complementing the model PP with potentials depending on the dipole α_d and quadrupole α_q core polarizability. The drawbacks of this method are the necessity of preliminary α_d and α_q determination (the accuracy of these calculations is usually not high) and the inadequate inclusion of the main exchange-correlation effects. Nevertheless, wide experience using model PP has shown that sometimes the results of correct *ab initio* many-electron calculations are reproduced with a rather high accuracy. In particular, this is true for molecules containing the atoms of the first two periods of the periodic table and transition metals [14-16]. Also of great importance is optimization of valence orbital bases (see [1, 2, 14]). Thus, the use of shortened valence bases often leads to unsatisfactory results. It is customary to assume direct optimization of PP in calculations of atoms to be the best way of valence function

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determination. The optimized function sets are given in [17, 18]. Comparison of the results of PP calculations with those of configuration interaction calculations shows an average error of the former for correlation effects to be ~10% or more. Probably the most suitable objects for PP calculations are the one-quasiparticle (having one electron over the core of filled electron shells) molecular alkaline ions M_2^+, M = Li, Na, K, Rb, Cs [16, 19]. In the case of several outer electrons (quasiparticles), the problem of including an accurate correction for the interelectron correlation becomes very important. Only with correct methods of its solution can the PP calculations be accurate enough. Some papers describe construction of correct *ab initio* valence Hamiltonians within the quasidegenerate perturbation theory and other approaches (see [1, 20-24]). In our opinion, a very proficient and consistent procedure is construction of model PP (Hamiltonians) within a perturbation theory of Rayleigh–Schrödinger type that effectively allows for the exchange-correlation effects as high-order effects and involves test PP of zero approximation. This method is successfully applied to atoms and ions [25-32], as well as to molecules [33-36].

This paper deals with the problem of PP calculations of homo- and heteronuclear diatomic alkaline molecules M_2, M = Li, Na, K, Rb, Cs. At present, interest in this problem remains very high due to the importance of information about these molecules in some applications, for example in laser and chemical physics, in plasma chemistry, and so on (see the recent paper [7] and [37, 38]). The model Hamiltonian for the system is constructed in the Rayleigh–Schrödinger perturbation theory using the test zero approximation PP. As the zero approximation PP, a local model potential of the Hellmann type [2] is used. Two main effects of the second-order perturbation theory are critical in obtaining an acceptable accuracy: the polarization interaction of valence particles via the core and their mutual screening. We report here original procedures for including corrections for these effects in the calculation. It is shown that in calculations of diatomic alkaline molecules in zero approximation of the perturbation theory with zero approximation PP, employment of empirical information about simpler corresponding ions makes it possible to improve the accuracy of calculations without additional calculation efforts.

ZERO APPROXIMATION

Within the PP approach, the problem of calculating the M_2 molecules (M = Li, Na, K, Rb, Cs) may be reduced to calculating the system consisting of two outer electrons (quasiparticles) moving in the inert gas ionic field of $M^+ - M^+$ forming the core. The ground state of the system (with two quasiparticles over the core in the second quantized representation) is

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

where a^+ is the creation operator for the particle over the core; Φ_0, the core state; and C, the angular symmetry coefficient. The electronic Hamiltonian of the system is

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

where ε_i are the one-quasiparticle energies, and

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

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

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

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

where R is the internuclear distance; and Z_a^c, Z_b^c are effective charges (see [39, 40]). The procedure of correct determination of Z^c is presented, for example, in [39]. As a model potential V_M, a local potential of the Hellmann

TABLE 1. Parameters of the Model Potential V_M (a.u.) and Experimental Ionization Energies of Alkaline Atoms (eV)

Atom	A	k	$-\varepsilon$
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

type [2] is used:

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

where A, k are parameters of the potential usually calibrated according to the experimental energies of the ground state of alkaline atoms (Table 1). The correct molecular model PP is represented as the sum

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

To realize the method of the perturbation theory with zero approximation PP, we should use the eigenfunctions of the known quantum mechanical two-center problem having the potential V_M as functions of zero approximation (see [38]). This will be done below for the Li_2 molecule as a variation of the calculations. Previously we have already dealt with the two-center problem (see [34], and also [41, 42]). As a second version we use the variation Rayleigh–Ritz principle, and as a test wave function we use a function of the form [16]

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

where λ, μ are ordinary prolate spheroidal coordinates, $\lambda = (r_a + r_b)/R$, $1 \le \lambda \le \infty$, $\mu = (r_a - r_b)/R$, $-1 \le \mu \le 1$; α, β are the variation parameters determined by minimization of the ground state energy; and n is an integer chosen so as to obtain the best energy (for details, see [16]). In this version, different homo- and heteronuclear types of alkaline molecules are considered. The third version of calculations is practically identical to the second one excluding the fact that the $\alpha(\beta, n)$ parameters are chosen to fit the experimental dissociation energy of the corresponding M_2^+ ion (in particular, Li_2^+). So the calculation of the M_2 system involves two steps:

1) construction of the model zero approximation using empirical information to determine the PP parameters; and

2) calculation of corrections of various orders of the perturbation theory employing the Rayleigh–Schrödinger perturbation theory and efficiently taking into account the exchange-correlation effects as effects of higher orders of the perturbation theory by using the corresponding one- and many-particle PP. The operator

$$H_{pT} = \sum_{\delta} \sum_{i,j} \left[r_{ij}^{-1} - V_M(r_{i\delta}) \right], \tag{4}$$

where δ, i, j are the dummy indices with respect to nuclei and electrons respectively, is assumed to be the perturbation operator.

CORRECTIONS OF VARIOUS ORDERS OF THE RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY

In [34, 36], the perturbation theory series for the secular operator matrix was built and methods of summing the diagrams for the states with nearly degenerate (in zero approximation) levels were considered. The terms of the series were represented as contributions of the Feynman diagrams classified according to the number of terminal lines (see Fig. 1). In accordance with this classification, the matrix element M of the secular operator was represented as

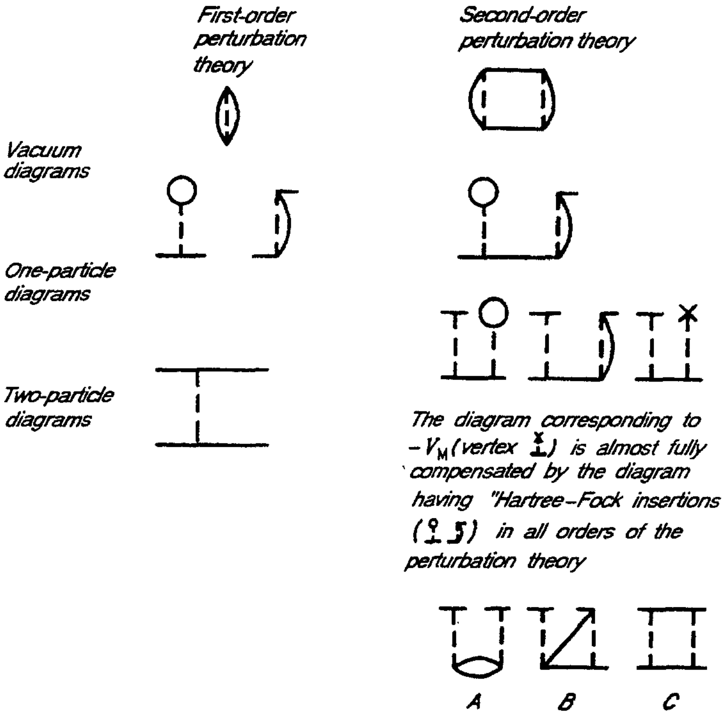

Fig. 1. Feynman diagrams of the perturbation theory with the model zero approximation pseudopotential.

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

where i is the total number of quasiparticles; $M^{(0)}$, the vacuum diagram (without terminal lines); $M^{(1)}$, the one-quasiparticle diagram (with a pair of terminal lines); $M^{(2)}$, two-quasiparticle diagrams (two pairs of terminal lines), and so on. The $M^{(0)}$ term defines the core energy. $M^{(1)}$ equals the sum of the one-quasiparticle states ε_i. In the first-order perturbation theory we should calculate only the contribution of the first-order two-quasiparticle diagrams that take into account direct Coulomb interaction of quasiparticles. The desired first-order correction equals the interaction energy of quasiparticles $\Delta E^{(1)}$ and is expressed via ordinary matrix elements using the wave functions of zero approximation. For the r_{12}^{-1} operator, we use here Neimann's expansion in terms of the associated Legendre polynomials of the first and second types and spherical harmonics (for details, see [42]). Note that the two-particle diagrams having a compensating term in H_{pT} $(-V_M)$ are absent in the first-order perturbation theory. Such diagrams arise in the second order but, as was shown by Tolmachev, for our case their contribution is substantially compensated by the contribution of the diagrams having the so-called proper energy insertions (see [27, 28]). Below we consider the second-order diagrams A, B, and C (see Fig. 1) for which the calculation should be done. In the theory of many-electron systems, the correlations are usually included in the calculation by adding some extra configurations, that is, by expanding the secular matrix. The additional configurations may be divided into two groups:

1) the states with excited core electrons (having one vacancy in the core and three electrons over the core); addition of these states permits us to include the polarization interaction of quasiparticles via the polarizable core (second-order diagrams in Fig. 1 A, B); and

2) the states with an excited outer quasiparticle, the number of outer particles remaining constant; with these states we can describe the mutual screening effect of outer particles (second-order diagram in Fig. 1 C).

The two state types give the correction of the second-order perturbation theory

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

Note that such an additive division is possible only in the second order of the perturbation theory; higher orders involve terms describing interference of these effects. The addition of states of the second type would lead to very cumbersome matrix elements. The states of the second type may be in principle included in the secular matrix using $\Delta E^{(1)}$ for a matrix element. However, it may appear that the whole continuum of high states will have to be included to get reliable accuracy. An effective way to include the states of both the first and the second types with the matrix size remaining constant (and without additional calculation efforts) was suggested in [34, 36]. It involves adding the polarization operator describing the interactions of outer particles via the polarizable core to the Coulomb operator of an interparticle interaction. According to [36c], the matrix elements of the polarization operator

$$\mathcal{F}_{\text{pol}}(r_1, r_2) = X\Big\{\int d^3r\rho_c^{1/3}(r)/|r_1 - r| \cdot |r - r_2| -$$
$$\Big[\int d^3r\rho_c^{1/3}/|r_1 - r| \times \int d^3r\rho_c^{1/3}(r)/|r - r_2|\Big]/\int d^3r\rho_c^{1/3}(r)\Big\} \qquad (5)$$

are the contributions of polarization diagrams (see Fig. 1). Here X is the numerical coefficient (its calculation technique is presented in detail in [36c]); ρ_c is the core electron density neglecting outer quasiparticles. The polarization correction for ρ_c was calculated using the ansatz $\rho_c = \rho_a + \rho_b$; $\rho_{a,b}$ were determined as in [43]. The general calculation procedure for $\Delta E_{\text{pol}}^{(2)}$ is described in [36c] (see also [34]). Note that the angular parts of matrix elements $r_{12}^{-1}\mathcal{F}(r_1, r_2)$ coincide; therefore, inclusion of the $\Delta E_{\text{pol}}^{(2)}$ correction amounts to modification of radial integrals entering the relation for $\Delta E^{(1)}$. Introduction of $\mathcal{F}_{\text{pol}}$ allowed us to reduce the problem to that of two particles interacting via potential $r_{12}^{-1} + \mathcal{F}_{\text{pol}}(r_1, r_2)$, now with an accuracy of the second-order perturbation theory.

The mutual screening effect of outer particles may be included by adding a screening potential W_{scr} arising due to the presence of the second particle to the interaction potential of the outer electron with all core electrons in the zero approximation Hamiltonian. The desired W_{scr} was chosen so that

$$\left\langle \left| \sum_{\delta} \frac{\theta}{r_{i\delta}} \right| \right\rangle = \langle |r_{12}^{-1}| \rangle,$$

where θ is the potential parameter (see below). In this case, the matrix elements are calculated using the wave functions of zero approximation with the test model potential. Alternative methods to include the screening effect are described elsewhere (see, for example, [30, 41]). Due to the zero-order W_{scr} we can effectively include the "ladder" diagrams in all orders of the perturbation theory (see Fig. 1).

CALCULATION RESULTS AND THEIR ANALYSIS

We report the dissociation energies of the diatomic molecules M_2 (M = Li, Na, K, Rb, Cs) calculated by the PP method in the Rayleigh–Schrödinger perturbation theory. Table 2 lists the test values of the α, β, n, N (N is the

TABLE 2. The $\theta, \alpha, \beta, n, N$ Values (N is the normalization constant), Equilibrium Distances R_e, and Dissociation Energies of Ions D_e (all values are in a.u., D_e in eV)

Ion	α	β	n	D_e	R_e	N	θ
Li_2^+	0.5044	0	2	0.97	6.29	0.3012	0.7239
	0.6111	0	3	0.95	6.36		
Na_2^+	0.4816	0	2	1.14	6.48	0.3777	0.7318
	0.5865	0	3	1.13	6.48		
K_2^+	0.4940	0	3	1.03	7.90	0.1444	0.7983
Rb_2^+	0.4731	0	3	0.86	8.4	0.1270	0.8149
Cs_2^+	0.4468	0	3	0.85	8.97	0.1465	0.8277
NaK^+	0.5332	0.0473	3	0.73	7.30	0.1249	0.7648
$NaRb^+$	0.5249	0.0576	3	0.60	7.53	0.1149	0.7752

TABLE 3. Dissociation Energies (eV) of M_2 molecules (M = Li, Na, K, Rb, Cs) Calculated in Various Approximations of the PP Method, and Experimental Data (see [4, 16, 37, 43, 44])

Molecule	*a*	*b*	*c*	*d*	*e*	*f*	*g*	*h*I	*h*II	*h*III	*k*	*l*
Li_2	1.05	1.57	–	–	0.24	0.89	–	0.98	0.92	0.97		
Na_2	0.74	1.33	0.25	0.23	0.25	–	0.59	–	0.68	–		
K_2	0.52	0.64	0.09	012	0.24	–	0.46	–	0.58	–	0.49	0.54
Rb_2	0.49	0.49	0.02						0.40	–	0.46	0.48
Cs_2	0.42	0.25	0.01						0.35	–	0.44	0.40
NaK	0.63	0.90	0.15						0.55			
NaRb	0.58	0.79	0.09						0.51			

Note. *a*) experimental data; *b*) Gaussian PP and model wave functions; *c*) Hellmann potential and Gaussian model wave functions; *d*) Hellmann potential and Heitler–London ansatz with Slater orbitals; *e*) Hartree–Fock potential plus the corrected Phillips–Kleinman PP and Heitler–London ansatz with Slater orbitals, with core polarization included in the form of an effective potential; *f*) model PP and 13-configuration wave function; *g*) model PP and the configuration interaction approximation using approximate natural orbitals; *h*) this paper: I, II, III are calculation versions (see text); *k*) the semiempirical approach of the perturbation theory (with fitting to experimental data); *l*) the local density approximation in the density functional theory.

normalization constant) parameters for the zero approximation wave function found by the variation technique for the corresponding molecular ions M_2^+ (see [16]) and the dissociation energies.

Naturally, $\beta = 0$ for homonuclear and $\beta \neq 0$ for heteronuclear cases. The θ values of W_{scr} (see above) are also given in Table 2. Table 3 presents the dissociation energies calculated for the lithium dimer in three variants (see above): 1) zero approximation functions are the functions of the quantum mechanical two-center problem; 2) the test wave function (3) with parameters determined by the variation technique (see Table 2); and 3) the test function (3) with the α parameter chosen to fit the experimental dissociation energy of Li_2^+. The exchange-correlation effects were included by the above-described procedure. Table 3 also contains the dissociation energies (variant 2) for diatomic alkaline molecules except Li_2. For comparison we give the dissociation energies calculated in different versions of the PP approach, particularly using the Gaussian, Phillips–Kleinman, and Hellmann PP and the wave functions in the Gaussian form, the Heitler–London ansatz having Slater orbitals, and multiconfiguration approximate natural orbitals. In this PP approach, an accurate correction for the effects of polarization interaction of outer quasiparticles via the core and the mutual screening of these particles is critical. The main conclusion inferred from comparison and analysis of these data is the need for an accurate method for inclusion of these effects in calculations of diatomic alkaline molecules. It is due to the inclusion of these effects in the Rayleigh–Schrödinger perturbation theory that the results obtained in this work are more precise than those of previous PP calculations. Apparently, on the basis of modern *ab initio* methods with correct inclusion of the configuration interaction one can obtain data of equal or even higher precision. However, this needs equivalent calculation efforts [20-22]. The analysis of calculations for the lithium dimer in three variants shows that the employment of eigenfunctions of the two-center problem in zero approximation as wave functions leads to more precise results than employment of model functions (3). Fitting the α parameter of (3) in the third variant of calculations for Li_2 to the experimental dissociation energy of Li_2^+ ($D_e = 1.29$ eV) leads to a more precise D_e value for Li_2 than in the case of variationally determined α. This is probably explained by the use of empirical data on simpler related systems in the zero-approximation perturbation theory. This method is well known from atomic theory, in particular, from calculations of the ground and excited atomic state in a similar approach (see [30, 31]). In terms of diagrams it means more adequate regard for the respective correlation diagrams. Of special interest is the use of this method for calculations of excited molecular states (solution of such problems involves considerable difficulties). Finally, due to the known progress in the *ab initio* quantum theory [22, 33], in particular, the *ab initio* PP theory, it seems appropriate to use the *ab initio* PP in zero approximation of the given perturbation theory method. This question, as well as the new *ab initio* approach to construction of the molecular PP (Hamiltonian) and a new principle of choosing the perturbation theory basis with zero approximation model PP based on the Hellmann–Low adiabatic formalism [45] (which is of particular interest for relativistic quantum chemistry) will be considered in a separate paper.

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