EXTENDED PSEUDOPOTENTIAL CALCULATIONS WITH GAUSSIAN-TYPE POLARIZATION POTENTIAL FOR ALKALI HOMO- AND HETERONUCLEAR DIATOMIC MOLECULES*

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We have calculated the valence energies and other properties of the alkali diatomic molecules. This paper presents a procedure to calculate the polarization effects in the valence energies of diatomic alkali molecules. Using the pseudopotential method we have introduced an approximate polarization potential consisting of a sum of four Gaussians fitted to Bardsley's potential. Some spectroscopic constants have been determined by using the Morse function. Total valence energies, internuclear distances, dipole moments, variational scaling parameters and constants are tabulated for homonuclear X_2 and heteronuclear XY ($X = Y =$ Li, Na, K, Rb, Cs) molecules.

The results for most of the properties are sufficiently good and give possibilities of further investigations.

Introduction

In a previous paper we have given an approximate form of the Bardsley's polarization potential and some results were presented for alkali hydride molecules as LiH, NaH, KH, RbH, CsH by using the pseudopotential method [1, 2]. In this paper we have extended the calculations for further alkali diatomic molecules. We have used the simplex method [3] for the determination of the scaling parameters and the Morse function for interpolation and evaluation.

The vibration–rotation energy levels, the vibration–rotation and pure rotation spectra in principle may be calculated from the geometrical and atomic data of the molecule and the shape of the potential energy function. Diatomic molecules specially have a simple relation between force constant in the potential energy function and the observed vibration–rotation spectrum. The spectroscopic constants in the theory of Morse potential are well investigated [4].

The procedure has the following steps: Variational calculation of scaling parameters using the simplex method starting from parameters of alkali hydrides. Calculations of Morse parameters and minimum of total valence energy together with the internuclear distance. Calculations of spectroscopic constants.

In addition, we have studied the influence of extending the original (sp)-basis with a single Gaussian bond orbital. In this paper atomic units are used.

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* Dedicated to Professor István Kovács on his eightieth birthday

Method of calculation, basis functions

In alkali atoms the interaction of core and one valence electron can be realized with the following pseudopotential:

$$V_{\text{pseu}}(r) = \sum_{l=0}^{l_{\max}} V_l(r) P_l, \qquad (1a)$$

where

$$V_l(r) = A_l \exp(-\gamma_l r^2). \qquad (1b)$$

This term is repulsive for $l \leq l_{\max}$, where $l_{\max}$ is the highest quantum number occurring in the core of the atom. This term represents in energy partly the effect of the orthogonality of the valence electron with the core electrons. A_l, γ_l are reasonable selected constants (Table I). In Eqs (1a) and (1b) r is the distance from the nucleus and P_l is the corresponding angular momentum projection operator.

Table I
Pseudo- and polarization parameters. Detailed definition is in [5]

	Li	Na	K	Rb	Cs
α_D	0.1925	0.945	5.47	8.966	15.0
α_Q	0.112	5.0	41.5	102.0	230.0
d	0.75	1.1	1.5	1.95	2.0
$l_{\max}$	2	2	2	3	3
A_0	6.013668	10.28159	9.568369	17.29503	14.76732
γ_0	1.293213	1.294506	0.709742	0.746748	0.541614
A_1	−0.740679	2.692467	2.897295	2.851747	2.960707
γ_1	1.410279	0.681447	0.363969	0.295391	0.232594
A_2	−0.067342	−1.452763	−3.916641	−1.553162	−0.399982
γ_2	0.8	1.0	0.748353	0.387761	0.193255
A_3	−	−	−	−1.380882	−1.943567
γ_3	−	−	−	0.436382	0.367542

The approximate polarization potential can be written as

$$V_{\text{pol}}^*(r) = -0.5\alpha_D^* S^2(r/d) - 0.5\alpha_Q^* S^3(r/d),$$

where

$$\alpha_D^* = \alpha_D/d^4 \quad \text{and} \quad \alpha_Q^* = \alpha_Q/d^6$$

and

$$S(y) = 1/(1+y^2) \simeq \sum_i a_i \exp(-\beta_i y^2) \quad (i = 1, \ldots, 4)$$

and $y = r/d$ and it takes well into account the polarization of the core. Here α_i, β_i are constants [1]. α_D and α_Q are the dipole and quadrupole polarizability, respectively.

The one-electron total potential is

$$U^*(r) = V_{\text{pseu}}(r) + V^*_{\text{pol}}(r) - Z/r,$$ (2)

where Z is the atomic number and the total potential energy for the AB alkali molecules is

$$U^*(r_A, r_B, Z_A, Z_B) = \sum_{i=1}^{2} \{U^*(r_{Ai}, Z_A) + U^*(r_{Bi}, Z_B)\} + \frac{1}{r_{12}} + \frac{Z_A Z_B}{r_{AB}}.$$ (3)

The set of basis orbitals included s and p orbitals simulated by linear combinations of spherical Gaussians and single Gaussians centered on the respective nucleus to take the effects of the pseudopotential's inner part into account and a single Gaussian on or near the point halving the distance of the two nuclei at point M. In calculations with these orbitals the internuclear distance was also a variational parameter.

A normalized spherical Gaussian orbital is defined as

$$\Phi_i(r) = (2a_i/\pi)^{3/4} \exp(-a_i r^2) = \left(\frac{2}{\pi \rho_i^2}\right)^{3/4} \exp\left(-\frac{1}{\rho_i^2} r^2\right).$$ (4)

Here we introduced the radius ρ_i of the orbital i by the relation $\rho_i^2 = 1/a_i$ which can be regarded also as a scaling parameter. Scaling parameters which generate the atomic orbitals are given in Tables II and III.

Table II

Znl, ρ_1, ρ_2 variational scaling parameters of alkali homonuclear molecules for (sp) basis functions with polarization. Old parameters of the alkali hydrides are in the first row, and new parameters are in the second row, ρ_M is the scaling parameter of a single Gaussian centered at M. For more information see Text

Znl	Li$_2$	Na$_2$	K$_2$	Rb$_2$	Cs$_2$
$Z2p$	0.5135	0.5267	0.5156	0.5816	0.6256
	0.6035	0.5451	0.5271	0.6236	0.6272
$Z3s$	1.0168	0.9698	0.9719	0.9268	0.8365
	0.8900	0.8743	0.8233	0.7849	0.7427
$Z3p$	1.8481	1.5855	1.8428	1.6213	1.4415
	1.6322	1.7109	1.9150	1.7084	1.5246
ρ_1	1.5319	1.6499	1.5223	1.5820	1.3350
	1.4239	1.5544	1.3844	1.5163	1.4553
ρ_2	2.0616	2.2557	1.5554	1.5918	2.0149
	2.7057	2.6589	1.5296	1.5691	2.0454
ρ_M	–	–	–	–	–
	3.1603	2.9384	2.7678	2.8925	2.9881

Table III

Znl, ρ_1, ρ_2 variational scaling parameters of heteronuclear molecules for (sp) basis functions with polarization. ρ_M is the scaling parameter of a single Gaussian centered at M.

Znl	LiNa		LiK	
	Li	Na	Li	K
$Z2p$	0.5586	0.5730	0.5368	0.5246
$Z3s$	0.9696	0.8960	0.8670	0.8667
$Z3p$	1.5963	1.7249	1.8788	1.9843
ρ_1	1.5237	1.6103	1.5308	1.6186
ρ_2	2.1093	2.2787	2.1259	1.6681
ρ_M	2.7588		3.0622	

Znl	LiRb		LiCs	
	Li	Rb	Li	Cs
$Z2p$	0.5566	0.6464	0.5903	0.6220
$Z3s$	0.8656	0.8460	0.8979	0.7818
$Z3p$	1.8388	1.6975	1.8858	1.4576
ρ_1	1.5158	1.6212	1.5510	1.3639
ρ_2	2.1412	1.6655	2.0569	2.0846
ρ_M	2.8098		2.6060	

Znl	NaK		NaRb	
	Na	K	Na	Rb
$Z2p$	0.5505	0.5323	0.5311	0.6032
$Z3s$	0.8306	0.8315	0.8823	0.8570
$Z3p$	1.7279	1.9341	1.6770	1.6470
ρ_1	1.5699	1.3982	1.6508	1.6507
ρ_2	2.6854	1.5448	2.3015	1.6693
ρ_M	3.0233		2.5479	

Znl	NaCs		RbCs	
	Na	Cs	Rb	Cs
$Z2p$	0.5648	0.6017	0.5955	0.6134
$Z3s$	0.8556	0.7692	0.7764	0.7990
$Z3p$	1.6778	1.4350	1.6529	1.4441
ρ_1	1.6124	1.4477	1.6501	1.4789
ρ_2	2.2565	2.2247	1.5227	2.2322
ρ_M	2.8586		2.8029	

Znl	KRb		KCs	
	K	Rb	K	Cs
$Z2p$	0.5202	0.5899	0.5347	0.6727
$Z3s$	0.8141	0.8353	0.7739	0.7894
$Z3p$	1.9284	1.6721	1.8317	1.3921
ρ_1	1.5549	1.5863	1.5581	1.4454
ρ_2	1.6273	1.6379	1.6677	2.1993
ρ_M	2.6744		3.0732	

Table IV

Valence energies E, dipole moments μ are presented at experimental internuclear distance R (first row) in ($spdf$) basis [1], and at calculated internuclear distance R, for diatomic homo- and heteronuclear molecules with variational scaling parameters, in (sp) basis (second row) and (sp) basis + single Gauss orbital with centrum in M (third row) with polarization. Parameters are in Table II and III. R, E in atomic units, μ in Debyes.*

Molecule	R	E	μ
Li$_2$	5.051089	−0.400199	−
	5.227272	−0.401688	−
	5.233239	−0.401836	−
LiNa	5.310170	−0.388984	0.275862
	5.497177	−0.389229	0.290627
	5.493868	−0.389588	0.269374
LiK	6.179450	−0.357691	3.187452
	6.292134	−0.357753	3.235211
	6.252397	−0.358520	3.212953
LiRb	−	−	−
	6.524533	−0.351618	3.872181
	6.497560	−0.352126	3.212953
LiCs	6.689680	−0.341248	4.857003
	6.885553	−0.341443	4.949802
	6.826615	−0.342002	4.976284
Na$_2$	5.818267	−0.378101	−
	5.767339	−0.378117	−
	5.759621	−0.378751	−
NaK	6.782280	−0.347474	2.831495
	6.512471	−0.347894	2.747736
	6.484870	−0.348494	2.757141
NaRb	−	−	−
	6.718018	−0.341119	3.365466
	6.672200	−0.341611	3.3547991
NaCs	7.558964	−0.330490	4.7991134
	7.152498	−0.331075	4.626502
	7.076763	−0.331938	4.6001149
K$_2$	7.379682	−0.317293	−
	7.210945	−0.317398	−
	7.186938	−0.317660	−
KRb	7.691240	−0.310632	0.887604
	7.426147	−0.310869	0.855182
	7.396925	−0.311111	0.877053
KCs	8.088100	−0.300247	2.326663
	7.856534	−0.300403	2.279516
	7.797916	−0.300930	2.370939
Rb$_2$	8.4093348	−0.295538	−
	7.658523	−0.305504	−
	7.630643	−0.305814	−

Table IV (continued)

Molecule	R	E	μ
RbCs	–	–	–
	8.035822	−0.294498	1.755712
	7.991324	−0.294777	1.847266
Cs$_2$	8.447143	−0.280272	–
	8.426512	−0.284619	–
	8.400547	−0.284833	–

* The experimental values of the dipole moments of the AB type
alkali molecules are in Debyes
LiNa $\mu = 0.463$, LiK $\mu = 3.4$, LiRb $\mu = 4.0$,
NaK $\mu = 2.667$, NaRb $\mu = 3.1$, NaCs $\mu = 4.75$.
Our calculated values clearly show the tendencies of the experi-
mental data (see [6]) and the agreement is very good.

Results and discussion

We have developed easily usable pseudopotentials with polarization poten-
tial for the alkali atoms. The calculations for the hydrides have shown that these
molecules can be described by a two-electron model. Even the Hartree–Fock SCF
self-consistent-field (SCF) calculations have given good results and the more com-
plicated models may give finer results. The total valence energies give a substantial
binding and the correlation energies are important but only a part of bonding en-
ergy.

In the AA and AB type alkali molecules the two-electron Hartree–Fock SCF
model gives only a little binding and the correlation energy gives most of the binding
energy. According our calculation, however, the equilibrium internuclear distances
and other properties are well described in this approximation.

In this paper we have calculated the valence energies and internuclear dis-
tances for homonuclear diatomic molecules AA of alkali atoms and for heteronuclear
diatomic molecules AB of alkali atoms. The results are presented in Table IV for
all of the alkali atoms in the periodic table together with the dipole moments. The
results are very encouraging if we observe that we are dealing with a two-electron
model in SCF approximation.

In Table V we are presenting results of calculations for vibration frequency ω,
rotation constants B and centrifugal distortion constants D for the same AA and
AB type alkali diatomic molecules. The agreement of the results of calculations
and the experimental data are very good.

The final conclusion is that further calculations with more involved models
especially those including correlation are very promising.

Table V

Vibration frequency ω, rotation constant B, and centrifugal distortion constant D are presented for diatomic homo- and heteronuclear molecules with variational scaling parameters, in (sp) basis set (second row) and (sp) basis set + single Gauss orbital with centrum in M (third row) with polarization. Parameters are in Table II and III. The experimental values are in the first row [6]. (ω, B in cm^{-1} and D in 10^{-8} cm)

Molecule	ω	B	D
Li$_2$	351.43	0.67264	985.66
	343.19	0.62804	841.27
	342.34	0.62661	839.71
LiNa	256.8	0.396	376.66
	258.84	0.370	303.87
	267.83	0.371	284.83
LiK	207.0	0.265	173.72
	211.0	0.256	150.17
	219.8	0.259	143.86
LiRb	185.0	–	–
	193.71	0.2182	110.76
	201.73	0.2200	104.70
LiCs	167.0	–	–
	197.1	0.1905	71.16
	191.7	0.1918	76.77
Na$_2$	159.124	0.1547	58.49
	163.395	0.1574	58.48
	170.342	0.1578	54.24
NaK	124.134	0.0905	19.27
	129.161	0.0981	22.68
	128.659	0.0990	23.45
NaRb	106.64	–	–
	116.21	0.0737	11.86
	114.69	0.0747	12.69
NaCs	98.0	–	–
	102.57	0.0600	8.22
	106.56	0.0613	8.12
K$_2$	92.021	0.0567	8.63
	98.845	0.0594	8.59
	102.681	0.0598	8.12
KRb	75.5	–	–
	83.59	0.0408	3.90
	83.99	0.0411	3.96
KCs	66.2	0.0305	2.60
	71.84	0.0323	2.62
	74.68	0.0328	2.54
Rb$_2$	57.31	0.0233	1.55
	62.05	0.0241	1.46
	64.61	0.0243	1.38
RbCs	49.41	–	–
	55.26	0.0179	0.76
	55.91	0.0181	0.77
Cs$_2$	42.022	0.0127	0.46
	45.459	0.0127	0.40
	46.37	0.0128	0.39

Acknowledgements

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