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Model analysis of ground-state dissociation energies and equilibrium separations in alkali-metal diatomic compounds

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Ground-state dissociation energies D_e and equilibrium distances R_e for the series of homonuclear alkali-metal diatomic molecules Li_2,Na_2, . . . , as well as those for six heteronuclear alkali-metal diatomic compounds, are evaluated on the basis of a simple valence-bond model. Each alkali-metal atom in a diatomic molecule is characterized by two quantities: a Gaussian parameter β_e of the valence-electron function and a valence-to-core "relative-size" parameter $\gamma \equiv (\beta_c/\beta_e)^2$, with β_c the Gaussian parameter for the core-electron charge distribution. For the homonuclear diatomic molecules, accurate results are obtained with a $2s$ Gaussian valence function $(r^2-a^2)G$ orthogonalized to the core. For each homonuclear diatomic molecule there exists an optimal (β_e,γ) set yielding values of D_e and R_e in practically quantitative agreement with experiment. The quantities β_e and γ exhibit the expected physical behavior over the series in that β_e decreases from Li_2 to Cs_2, and γ is highest for the lightest diatomic molecule Li_2. The compounds K_2, Rb_2, and Cs_2 are found to be "Heitler-London" molecules to within 5% of their binding energies. An approximate, similar, analysis of six heteronuclear diatomic compounds yields close agreement with experiment for LiNa and RbCs, whereas with the other four compounds (LiK, NaK, NaRb, and NaCs) the agreement with experimental D_e and R_e is to within at most 5%. Also RbCs is a "Heitler-London" molecule to a very good approximation.

I. INTRODUCTION

In recent years there has been an upsurge in research on alkali-metal di- and polyatomic compounds (Li_n, Na_n, etc., also of mixed composition) for several reasons. One incentive has been the possibility of studying two-photon processes[1-4] (ionization, dissociation, and excitation) in the diatomic molecules with lasers in the visible spectral region. Also, cw alkali-metal dimer lasers have recently been realized. The present high accuracy of laser spectroscopy has made it possible, for example, to determine ionization potentials[5] of alkali-metal atoms and diatomic molecules to within a few cm^{-1}. For the diatomic molecules, on which we will concentrate in the present paper, the experimental ground-state dissociation energies range from 24 kcal/mole for Li_2 to 10 kcal/mole for Cs_2; the equilibrium distances lie between 2.7 Å (Li_2) and 4.6 Å (Cs_2). Thus, bonding in these compounds, although much weaker than in H_2 (109.5 kcal/mole), is considerably stronger than in so-called "van der Waals complexes" (a few kcal/mole).

On the theoretical side, the development of extensive methods has led to numerous applications in alkali-metal diatomic molecules (and some small-size clusters), also as a test of the validity of different approximation methods. All-electron SCF (self-consistent field) and valence-electron CI (configuration interaction) as well as MC (multiconfiguration) SCF methods are now of common use with the alkali-metal diatomic compounds, as exemplified by the MC SCF work on Li_2 (Ref. 6) and Na_2 (Ref. 7) by Konowalow *et al.*, followed by a number of analyses of similar complexity on these and other members of the series. It was found that, especially for the heavier atoms (from potassium onwards), intershell correlation poses a stumbling block because of slow convergence (see, e.g., Ref. 8). The correlation complication was circumvented by Müller and Meyer,[9] who introduced a (dipolar) core-polarization potential (CPP) developed by these authors and Flesch,[10] containing an atomic parameter (cutoff radius) which was determined such as to reproduce the experimental ground-state ionization potential of the atom. Their results (using a valence CI method, plus CPP) for the ground-state properties of Li_2, Na_2, K_2, and LiNa differ from experimental data by only 1—2 %.

On the other hand, to take full advantage of the particularly simple electronic structure of alkali-metal atoms (one valence electron well outside a closed inner shell), a great many theoretical studies have been based on pseudo- or model potentials to represent the cores. These are either determined from experimental valence-electron atomic spectra, or constructed nonempirically (SCF-adjusted). For heavy atoms, relativistic contributions to nonempirical pseudopotentials have been included. The paper by Müller and Meyer[9] contains a thorough analysis of the characteristics of such calculations.

Preuss and collaborators[11-15] incorporated the Müller-

Flesch-Meyer core-polarization potential in their pseudopotential calculations on alkali- and noble-metal compounds. In its most detailed version (for large cores as with Cu and Ag), there are five parameters per atom, determined such as to reproduce experimental excited—to—ground-state atomic energy differences, and the calculated (SCF) frozen-core Dirac-Fock ionization energies of the atoms. For alkali-metal diatomic molecules the complexity is not quite this large, since the approximation of nonoverlapping cores is found to hold to good approximation. This reduces the number of adjustable parameters per atom to three, plus a summation over angular momenta. A discussion of still other approaches to core-polarization and correlation effects, e.g. of a perturbation analysis by Jeung *et al.*[16] in conjunction with SCF-adjusted pseudopotentials, is found in the paper by Müller and Meyer.[9] The most detailed pseudopotential analyses generally yield binding energies with an accuracy of 0.1—0.2 eV and equilibrium distances differing by about 0.05 Å from experiment. For full details we refer the reader to the literature quoted.

Little effort has been undertaken in the literature over the past 50 years with the aim of providing insight into the binding characteristics of the whole *series* of alkali-metal diatomic compounds. Recently, Pelissier and Davidson[17] applied a nonorthogonal configuration interaction method to these molecules. The atomic orbitals forming the basis were expanded in large sets of Gaussian functions. Besides the calculated full CI values for D_e and R_e, a decomposition of the binding energy was performed in terms of contributions of different types (ionic terms, *s*-*p* excitation) for the series H_2, Li_2, Na_2, and Cs_2. These authors find a large contribution of *s*-*p* excitation. They also deduce that valence—other-core overlap constitutes the principal difference between binding in H_2 and in the alkali-metal diatomic molecules. Their full CI values for D_e amount to 79 (H_2), 71 (Li_2), 72 (Na_2), 76 (K_2), and 53 (Cs_2) percent of the experimental values. Although the agreement is quantitatively rather poor, the results account qualitatively for the observed decrease in binding energy going from Li_2 to Cs_2.

In spite of these advances, full-scale *ab initio* analyses resulting in (close to) experimental accuracy are limited to the lightest alkali-metal diatomic molecules, whereas pseudopotential approaches still necessitate large basis sets and extensive parametrization, thereby losing part of their advantage in principle. This raises the question whether such large-scale calculations are appropriate, and sufficiently accurate, for the evaluation of interactions in, or below, the millihartree domain. Davis and Monkhorst[18] constructed molecular basis functions for the hydrogen molecule from combinations of up to 40 Slater functions, with the aim of finding criteria for basis sets yielding energies accurate to below 1 millihartree (≤ 0.5 kcal/mole). Their attempt was not successful, and the authors conclude that it might be more profitable to pursue *methods that do not rely on basis sets.*

Already in 1934, a valence-bond treatment of Li_2 was carried through by James,[19] following the Wang-Rosen[20,21] analysis of the hydrogen molecule, with a distance-dependent exponential parameter in a 2*s* Slater function for the Li valence electron. The calculated dissociation energy was, however, much too low, accounting for only 20% of the experimental value (at an assumed separation of 2.78 Å). A subsequent variational treatment by the same author,[19] modeled after the James-Coolidge analysis[22] of H_2, but without the r_{12} correlation terms in the variation function, yielded a binding energy still too low by about 50%. Recently,[23] we calculated the ground-state binding energy and equilibrium distance of the hydrogen molecule using (simple) Gaussian wave functions for the atoms, with distance-dependent exponential parameters, i.e., without the use of basis sets. In the present paper a similar approach will be formulated for the alkali-metal diatomic molecules.

II. THE MODEL

We consider a system of two (identical) alkali-metal atoms A and B, in a two-electron description (valence electrons 1 and 2), at a distance R from each other, and write down the expectation value (E) of the total Hamiltonian H_{tot} in a valence-bond approach. Let the one-center wave functions for the valence electrons be ψ_A and ψ_B, respectively. We write $H_{\text{tot}}=H_0+V$, with H_0 the Hamiltonian for the noninteracting atoms and with V their Coulomb interaction. For the singlet state of the system we obtain directly for E, with $\langle\ \rangle$ referring to the simple product $\psi_A^{(1)}\psi_B^{(2)}$, and with Δ the overlap integral

$$\begin{aligned} E &= \langle (I+P_{12})H_{\text{tot}}(I+P_{12})\rangle/2(1+\Delta^2) \\ &= \langle H_{\text{tot}}(I+P_{12})\rangle/(1+\Delta^2) \\ &= \langle H_0\rangle + \langle V(I+P_{12})\rangle/(1+\Delta^2) \\ &\quad + [1/(1+\Delta^2)](\langle H_0P_{12}\rangle - \langle H_0\rangle\langle P_{12}\rangle)\,, \end{aligned} \tag{1}$$

where I is the identity operator and P_{12} permutes the labels of the valence electrons (thus $\langle P_{12}\rangle=\Delta^2$). The first term on the right of (1) is the expectation value $\langle H_0\rangle$ for two noninteracting atoms, the second term is of the same form as the Heitler-London (HL) interaction energy, and the last term contains "exchange corrections" to $\langle H_0\rangle$. This term is zero if ψ_A and ψ_B are eigenfunctions of H_0; the second term is then the so-called "exact HL energy."

In the first instance we choose, as for the hydrogen molecule,[23] 1*s* Gaussian functions

$$\psi_A(1)=(\beta/\pi^{1/2})^{3/2}\exp(-\beta^2 r^2_{1A}/2)\,,$$

and similarly for $\psi_B(2)$, with characteristic parameter β, to be determined. Equation (1) can now be readily evaluated. The results for the three terms of the sum are, respectively,[23]

$$\langle H_0\rangle=(3\hbar^2/m)\beta^2-2e^2\beta(2\pi^{-1/2})\,, \tag{2}$$

$$\langle V(I+P_{12})\rangle/(1+\Delta^2)=e^2\beta\{1/\beta R+[1/(1+\Delta^2)][-2\,\mathrm{erf}(\beta R)/\beta R+2^{-1/2}\mathrm{erf}(2^{-1/2}\beta R)/2^{-1/2}\beta R] +[\Delta^2/(1+\Delta^2)][-2\,\mathrm{erf}(\tfrac{1}{2}\beta R)/\tfrac{1}{2}\beta R+2^{1/2}\pi^{-1/2}]\}\ , \tag{3}$$

$$[1/(1+\Delta^2)](\langle H_0P_{12}\rangle-\langle H_0\rangle\langle P_{12}\rangle)=-(\hbar^2/2m)[\Delta^2/(1+\Delta^2)]\tfrac{1}{2}\beta^4R^2 +[\Delta^2/(1+\Delta^2)]e^2\beta[2^2\pi^{-1/2}-2\,\mathrm{erf}(\tfrac{1}{2}\beta R)/\tfrac{1}{2}\beta R]\ . \tag{4}$$

To simplify the notation, we abbreviate the sum of (2), (3), and (4) by $F(\beta,R)$. A relation between β and R at the minimum (fixed β) of F is obtained from $[\partial F(\beta,R)/\partial R]_\beta=0$. This relation is very close to a hyperbola $\beta R=C$, with $C=1.2748$ [the value 1.2748 is exact on the basis of the Heitler-London part of $F(\beta,R)$, i.e., Eq. (3)]. Small deviations (a few percent at most) occur for $R\leqq 0.8$ Å, thus for $\beta\geqq 1.6$ Å^{-1}; for the hydrogen molecule[23] the precise value is 1.3105. As in the case of H_2, we will interpret $\langle H_0\rangle$, Eq. (2), in the model as defining the zero of interaction.

In applying the same formalism to the alkali-metal diatomic molecules, we observe that the terms in Eq. (1) involving the *single-atom* operator H_0 are overestimated without appropriate scaling, since the hydrogenic model imposes that $\langle H_0\rangle$ depends on the principal quantum number n of the valence electrons as $1/n^2$. We now generalize the model treatment through the condition that the kinetic-energy part of $\langle H_0\rangle$, i.e., the first term of (2), must be equal to $(3\hbar^2/m)\beta^2/n^2$, the potential part of $\langle H_0\rangle$ [second term of (2)] equal to $-2e^2\beta(2\pi^{-1/2})/n^2$ for $n=1,2,\ldots,6$. The same scaling pertains to the two parts of Eq. (4).

With the above procedure, $1s$ Gaussian functions can be applied to the series of alkali-metal diatomic molecules. In Table I, the results of the calculations are given. The β values for the alkali-metal atoms were determined, in first approximation, from $\beta R_{\mathrm{expt}}=1.3105$ (H_2), where R_{expt} is the experimental equilibrium distance in the dimer; R_e and D_e are the calculated equilibrium distances and dissociation energies ($E-\langle H_0\rangle$ at $R=R_e$), and $-E_{\mathrm{HL}}$ is the Heitler-London part, Eq. (3), of D_e.

As it is seen from the table, the model results for D_e are in rather good agreement with experiment for Li_2, but they are too high for the other dimers; the R_e values agree with experiment to within only a few percent, and may thus be considered satisfactory. Surprisingly, however, the Heitler-London contributions are always *larger* than D_e. The β values in Table I also give a measure for the relative overestimate of $\langle H_0\rangle$ in the absence of scaling. If we compare Li and Cs, then without scaling (taking in first approximation for the β values those of Table I) the kinetic energy (proportional to β^2) decreases by a factor $(0.282/0.490)^2=0.33$, whereas according to the $1/n^2$ rule, this factor should be $0.33\times(2^2/6^2)=1/27$.

III. BINDING ENERGIES WITH CORE-ORTHOGONALIZED VALENCE FUNCTIONS

The results of the previous section show that to obtain binding energies of the alkali-metal dimers which are significantly better than those calculated with $1s$ Gaussian functions, the *atomic cores* must be taken into account explicitly. This is most simply accomplished through *orthogonalization*[24] of each valence function to that of its core. For the wave function of the core we choose a simple Gaussian G_c, with a parameter β_c, to be determined, to represent the core electrons collectively. The core orbital is occupied by two spin-paired electrons.

This procedure was first carried out for a $1s$ Gaussian valence function G, Schmidt-orthogonalized to the simple-Gaussian core function G_c. The orthogonal valence function ψ_v then reads, with Δ the overlap integral between G and G_c (both Gaussians normalized to one)

$$\psi_v=(1-\Delta^2)^{-1/2}(G-\Delta G_c)\ , \tag{5}$$

where

$$\Delta=[2\gamma^{1/2}/(\gamma+1)]^{3/2}\ , \tag{6}$$

with

$$\gamma\equiv(\beta_c/\beta)^2\ .$$

The parameter γ is a measure of the relative extension of the $1s$ Gaussian part of the valence function and that

TABLE I. Model values of the equilibrium distance R_e (in Å) and the dissociation energy D_e (in kcal/mole) for the homonuclear compounds Li_2, Na_2, K_2, Rb_2, and Cs_2, with $1s$ Gaussian valence-electron functions (parameter β), as compared with experiment. Also given are the Heitler-London component $-E_{\mathrm{HL}}$ of D_e and the value of the $1s$ Gaussian parameter β (in Å^{-1}) for each atom.

Compound	R_e	D_e	$-E_{\mathrm{HL}}$	β	R_{expt}[a]	D_{expt}[a]
Li_2	2.6	23.34	25.42	0.490	2.673	24.37
Na_2	3.0	21.32	22.20	0.428	3.079	17.22
K_2	3.9	16.86	17.29	0.334	3.924	12.00
Rb_2	4.1	16.02	16.29	0.314	4.170	11.30
Cs_2	4.7	14.34	14.52	0.282	4.648	10.42

[a] Detailed references are given in Table II.

of the core; $\gamma > 1$ in all systems considered.

We then choose values for the parameter β of the valence function, and values for the parameter γ. A scanning procedure *may* then yield sets (β,γ) which lead to R_e, D_e values close to experiment.

The dissociation energies are now found to be *lower* than the experimental values, by about 10%, in contrast with the nonorthogonalized 1*s* Gaussian functions (Table I). The equilibrium distances are between 5% and 10% lower than the experimental values; furthermore, best results for *all* compounds are obtained with $\gamma \cong 20$, a physically unlikely result.

Consistently good results for the whole series of homonuclear alkali-metal diatomic molecules were obtained by using a valence function $(r^2-a^2)G$, with Gaussian parameter β. This function, orthogonalized to G_c, may be considered the "2*s*" to the 1*s* Gaussian G. Orthogonalization yields the simple relation

$$\beta^2 a^2 = 3/(1+\gamma) \,, \tag{7}$$

where γ is the "relative-size" parameter, $\gamma = (\beta_c/\beta)^2$. We then evaluate the quantity $E - \langle H_0 \rangle$, Eq. (1), applying the scaling procedure to the terms occurring in Eq. (4) in the same way as outlined for the case of 1*s* Gaussian valence functions. Explicitly, the kinetic energy part of $\langle H_0 \rangle$ for a function $(r^2-a^2)G$ reads

$$\langle H_0 \rangle_{\text{kin}} = \frac{\frac{33}{32} - \frac{3}{8}\beta^2 a^2 + \frac{3}{8}\beta^4 a^4}{\frac{15}{16} - \frac{3}{4}\beta^2 a^2 + \frac{1}{4}\beta^4 a^4} (\hbar^2 \beta^2/2m)$$

$$\equiv K(\gamma)\hbar^2\beta^2/2m \,. \tag{8}$$

The function $K(\gamma)$ varies slowly with the relative-size parameter γ; for $\gamma \to \infty$ it is equal to 1.1, for $\gamma = 24$ it is 1.15, for $\gamma = 9$ it amounts to 1.30 and for $\gamma = 2$ it reaches the value 2.35. We scale $\langle H_0 \rangle_{\text{kin}}$ by a factor S_{kin} through the condition

$$S_{\text{kin}} K(\gamma) = 3/2n^2 \,. \tag{9}$$

It is found, as in the case of 1*s* Gaussian functions, that S_{kin} is practically equal to $1/n^2$ for the range of γ values (9—25) for the alkali-metal dimers.

The corresponding equation for the potential part $\langle H_0 \rangle_{\text{pot}}$ reads

$$-\langle H_0 \rangle_{\text{pot}} = \frac{\frac{1}{2} - \frac{1}{2}\beta^2 a^2 + \frac{1}{4}\beta^4 a^4}{\frac{15}{16} - \frac{3}{4}\beta^2 a^2 + \frac{1}{4}\beta^4 a^4} (2\pi^{-1/2} e^2 \beta)$$

$$\equiv L(\gamma)(2\pi^{-1/2} e^2 \beta) \,. \tag{10}$$

Also $L(\gamma)$ varies slowly with γ; for $\gamma \to \infty$ it is 0.53, for $\gamma = 24$ it is 0.52, for $\gamma = 9$ it amounts to 0.51 and for $\gamma = 2$ it reaches the value 0.57. We scale $\langle H_0 \rangle_{\text{pot}}$ by a factor S_{pot}, through the condition

$$S_{\text{pot}} L(\gamma) = 1/n^2 \,. \tag{11}$$

The scaling factors are then also applied to the two terms of Eq. (4), i.e., those containing the single-atom operator H_0.

After applying the scaling we use a scanning procedure and calculate dissociation energy and equilibrium separations for different sets of β_e, γ values. For the homonu-

TABLE II. Optimal model values for the valence Gaussian equilibrium parameter β_e (Å^{-1}) and the valence-to-core relative-size parameter γ in the orthogonalized function $(r^2-a^2)G$, for homonuclear and heteronuclear alkali-metal diatomic compounds. Also given are the calculated equilibrium distances R_e (Å), the dissociation energies D_e (kcal/mole), and the Heitler-London parts $-E_{\text{HL}}$ of D_e. In the last two columns, values for the dimensionless quantity $\beta_e R_e$ are listed.

	Optimal values		Model		Calculated	Experimental		Model
Diatomic	β_e	γ	D_e	R_e	$-E_{\text{HL}}$	D_e	R_e	$\beta_e R_e$
Li_2	0.760	24	24.38	2.64	18.44	24.37[a,b]	2.673[a]	2.00
Na_2	0.678	12.4	17.22	3.06	15.30	17.22[c,d,e]	3.079[c,d,e]	2.07
K_2	0.538	9.1	12.00	3.94	11.42	12.00[c]	3.924[f]	2.12
Rb_2	0.505	10.0	11.29	4.19	10.95	11.30[g]	4.170[h]	2.12
Cs_2	0.454	11.8	10.37	4.63	10.18	10.42[i]	4.648[j]	2.10
LiNa	0.710[k]	17	20.33	2.87	16.71	20.29[l]	2.885[l]	2.04
LiK	0.630[k]	16	17.16	3.25	14.64	17.59±0.35[m]	3.322[m]	2.05
NaK	0.616[k]	11.5	14.93	3.39	13.73	15.07[n,o]	3.498[n]	2.09
NaRb	0.608[k]	11.5	14.55	3.45	13.55	15.05[p]	3.558[p]	2.09
NaCs	0.575[k]	11.9	13.73	3.64	12.90	14.16[q]	3.850[q]	2.09
RbCs	0.482[k]	11.2	10.97	4.37	10.70	10.96[r]	4.37[r]	2.11

[a] Reference 25.
[b] Reference 26.
[c] Reference 27.
[d] Reference 28.
[e] Reference 29.
[f] Reference 30.
[g] Reference 31.
[h] Reference 32.
[i] Reference 33.
[j] Reference 34.
[k] β_e(MN) determined through independent scanning.
[l] Reference 35.
[m] Reference 36.
[n] Reference 37.
[o] Reference 38.
[p] Reference 39.
[q] Reference 40.
[r] Reference 41.

clear compounds the choice of the optimal β_e,γ values follows from the criterion of obtaining the closest agreement between the calculated and the experimental values of D_e. This criterion leads to calculated equilibrium separations which differ from experiment by -1.1% (Li_2), -0.6% (Na_2), $+0.4\%$ (K_2), $+0.4\%$ (Rb_2), and -0.4% (Cs_2). These optimal β_e,γ values giving very good agreement with *both* the experimental dissociation energy and the equilibrium separations, are reported in Table II for the homonuclear alkali-metal diatomic compounds, and for the heteronuclear compounds LiNa, LiK, NaK, NaRb, NaCs, and RbCs. For the latter category, only *one* β and *one* γ variable were used, in order not to complicate the model. We have also listed the Heitler-London contributions $-E_{\rm HL}$ and the values for the dimensionless product $\beta_e R_e$.

From the table we see that the function $(r^2-a^2)G$ yields indeed very accurate results for the whole homonuclear series. The fact that γ increases somewhat from K_2 to Cs_2 (from 9.1 to 11.8) may be due to the fact that only for nonorthogonal (1s Gaussian) valence and core functions $\gamma=(\beta_c/\beta)^2$ is a "true" relative-size parameter. In addition, deviations from the hydrogenic model adopted, and relativistic effects (shrinkage of valence orbitals) may play a role with the heavy diatomic molecules.

The Heitler-London contributions to the bonding are much more satisfactory than those found in the case of 1s Gaussian (cf. Table I). They amount to 76% for Li_2, of the same order as for H_2 (78%), and to 89%, 95%, 97%, and 98% for Na_2, K_2, Rb_2, and Cs_2, respectively. According to the model the heavier alkali-metal diatomic molecules are, therefore, "Heitler-London molecules" to a very good approximation.

For the heteronuclear compounds listed in Table II we have taken, as we mentioned, *one* variable β and *one* variable γ. Excellent agreement with the experimental R_e,D_e values is obtained for LiNa and RbCs, i.e., for the lightest and heaviest heteronuclear diatomic molecules, respectively. Here, the optimal values of β_e are very close to the arithmetic mean of the β_e in their homonuclear compounds. With LiK, NaK, NaRb, and NaCs we find deviations of a maximum of 5%. The approximation of using one variable β,γ set, may be too crude in these cases.

Finally, we have verified that the alternative criterion for choosing the optimal β_e,γ values, based on the closest agreement between calculated and experimental equilibrium separations, leads to optimal β_e,γ values which are very close to those listed in Table II. In the case of Li_2, with $\beta_e=0.755$ Å^{-1} and $\gamma=23$, one obtains $R_e=2.67$ Å and $D_e=23.61$ kcal/mole, with an error of -3% of the dissociation energy. We note that the product $\beta_e R_e$ remains practically constant for the two sets of optimal β_e,γ values.

IV. CONCLUDING REMARKS

From the analysis presented in this paper, a strikingly simple interpretation emerges regarding the effect of core electrons on ground-state dissociation energy (D_e) and equilibrium separation (R_e) of homonuclear alkali-metal diatomic compounds. Excellent agreement with experiment is obtained for D_e and R_e in a two- (valence-) electron model by choosing 2s Gaussian orbitals $(r^2-a^2)G$ for these electrons. Here G is a simple Gaussian function with characteristic parameter β, and a^2 is chosen such that the valence function is orthogonal to the simple Gaussian core function G_c, yielding $\beta^2a^2=3/(\gamma+1)$, with a relative-size parameter $\gamma=(\beta_c/\beta)^2$.

We have concentrated on *equilibrium* properties of the alkali-metal diatomic compounds (D_e,R_e,β_e,γ). In principle, it would have been possible to construct the complete potential $E-\langle H_0\rangle$, as was carried through for the hydrogen molecule[23] (Fig. 3 of Ref. 23), by minimizing $E\equiv\langle H_{\rm tot}\rangle$ of Eq. (1) with respect to all variables. However, it seemed more judicious to test the model first with respect to its accuracy at the equilibrium configurations.

The values for the dimensionless parameter $\beta_e R_e$ are quite close over the whole series of alkali-metal diatomic compounds (Table II), with a maximal deviation of 4% from a mean of 2.08. If we impose the condition

$$\langle r^2\rangle_{{\rm simple}\ G}=\langle r^2\rangle_{(r^2-a^2)G}\ ,$$

with parameter β' for the simple Gaussian, the $\beta'_e R_e$ is found to lie between 1.29 and 1.34 over the whole series. It is interesting to note that these values practically coincide with the corresponding value 1.31 obtained earlier[23] for the hydrogen molecule.

The set of β_e,γ values for each alkali-metal diatomic molecule obtained from the analysis implicitly contains effects such as valence-core polarization (same, or other, core), relativistic effects, etc. It is anticipated that such information provided by the model may prove adequate when we consider (weak) bonding in more complicated molecules and in small clusters of metal atoms.

The analysis presented thus far applies for homonuclear diatomic compounds (for the six heteronuclear systems we adopted the approximation of taking a single β,γ set of variable parameters). An important question concerns the possibility of formulating an analogous approach for the case of strongly heteronuclear diatomic compounds. Here, the alkali-metal hydrides are an obvious choice. This analysis is under way; the results will be published separately.

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