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Basis-independent potential energy curves for the neutral diatomics of Li, Na and K evaluated by means of Hartree–Fock and different density functional potentials

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Summary. The solution of the Schrödinger equation for diatomic molecules when the finite element method is used gives the possibility to evaluate highly accurate basis-independent potential energy curves. In this work such types of numerically accurate potential energy curves on the HF level have been evaluated for Li_2, Na_2 and K_2 and could be used as benchmarks in the optimization of basis sets. A comparison between recent LCAO HF calculations in which extended basis sets are used and the accurate values determined in this work show that there is a difference in total energy of 4×10^{-5} and 10^{-3} a.u. for Li, Li_2, and Na, Na_2, respectively. Evaluated dissociation energies are, however, due to the cancellation of numerical errors in much better agreement. Further, it is found that different exchange correlation potentials for the heavier molecules such as those given by von Barth–Hedin and Vosko, Wilk and Nusair reproduce experimental properties such as dissociation energies, vibrational frequencies almost as well as those achieved with advanced CI methods. The $X\alpha$ potential gives accurate bond lengths for Na_2 and K_2, whereas the dissociation energies are too small.

Key words: Neutral diatomics – Basis-independent potential energy curves – Li_2 – Na_2 – K_2

Access to experimental techniques for the production and study of metal clusters [1–5] has challenged theoreticians to test different *ab initio* and first-principle methods [6–9] for these types of molecules. A crucial problem in many of these calculations is the choice of suitable basis sets in the expansion of the molecular wavefunctions in a Molecular Orbital Linear Combination of Atomic Orbital, MO-LCAO, approach [10, 11]. Therefore the results can, in many cases, become limited by the chosen basis sets [12], although the Hamiltonian, which is defined by the chosen exchange correlation potential or the expansion terms in a Configuration Interaction, CI, or Many Body Perturbation Theory, MBPT, calculation, provide an accurate description. The use of very extensive basis sets is also limited by the n^4 problem for the two-electron potentials in HF-based methods and by the n^3 problem in density functional methods.

However, calculations of two-dimensional problems such as diatomic molecules can nowadays be done by means of pure numerical schemes such as the finite difference method, FDM, [13], and the finite element method, FEM, [14–16]. In the case of FEM, the Hamiltonian for the diatomic molecule is rewritten in ellipsoidal coordinates. The space defined by this representation is further divided into small domains, called the finite elements, on which *local basis functions* are defined, as opposed to the *global basis sets* used in the conventional basis-set expansions. The local basis functions are chosen as two-dimensional polynomials of the order 6 to 8, such that the expansion coefficients determined can be interpreted as the values of the unknown functions at a particular grid point.

In our groups so far, FEM calculations have been performed for the two-dimensional solution of the Hartree–Fock–Slater, HFS, [14, 15, 17, 18], spin-polarized HFS [19] and for restricted Hartree–Fock [20] equations for atoms and diatomic molecules. The numerical accuracy achieved in these calculations is of the order of 10^{-8} a.u., corresponding to 3×10^{-7} eV for the eigenvalues, total energies and dissociation energies. A detailed description of the application of the Finite Element Method for this type of quantum mechanical calculations has been given in our earlier work [14, 20].

To date, a number of calculations have been performed on small clusters of Li, Na and K in which different types of semiempirical and *ab-initio* methods have been used, see summaries in different reviews [6–9]. When molecular calculations are based on basis-set expansions the appropriate basis sets have usually been optimized by calculations for the corresponding dimers. In order to test the accuracy of these types of calculations we have evaluated numerically highly accurate potential energy curves for Li_2, Na_2 and K_2 within the HF method and also used different types of exchange correlation potentials, such as the $X\alpha$ [21], von Barth–Hedin, BH, [22], Vosko, Wilk and Nusair, VWN, [23]. Access to these types of accurate potential energy curves gives both the possibility to analyze the effect of basis-set errors and to test the accuracy of a number of exchange correlation potentials.

A summary of the total energies for the atoms and diatomic molecules at the equilibrium bond distance is given in Table 1. Different exchange correlation potentials and the Hartree–Fock are used. The molecular calculations have been carried out for internuclear bond distances ranging from 3 to 10 a.u. The results agree well with the one-dimensional calculations for the atoms calculated by Froese Fischer [24], see Table 1. Improved basis-dependent calculations were carried out for Li, Na and the diatomic molecules Li_2, Na_2 [25] in which recently determined basis sets [26] for the first- and second-row atoms were used, see the results given in the last column of Table 1. These basis sets for the first- and second-row atoms have been constructed by averaging over several atomic states, positive and negative ions, and atoms in an external electric field. The basis sets are characterized as (14*s* 9*p* 4*d* 3*f*) for Li and (17*s* 12*p* 5*d* 4*f*) for Na. There is a difference of 3×10^{-5} a.u. for Li and Li_2 to the highly accurate total energy values in column 4, whereas the difference is 7×10^{-4} and 14×10^{-4} a.u. for Na and Na_2. As a comparison, Bonačić-Koutecký et al. [27] obtained the total energies −7.432669 a.u. and −14.871098 a.u. for Li and Li_2 using a basis of the type (13*s* 3*p* 1*d*/6*s* 3*p* 1*d*) and the corresponding total energies for Na and Na_2 [28] were −161.84541 a.u. and −323.689982 a.u. with a basis of the type (14*s* 8*p* 1*d*/6*s* 5*p* 1*d*). For Na_2, the difference in total energy between the accurate values calculated in this work and the values evaluated with the new basis

Table 1. Summary of total energies in a.u. for the neutral Li, Na, K atoms and the corresponding diatomics evaluated by means of different exchange correlation potentials

Atom/molecule	$X\alpha$, $\alpha = 0.7$	BH	VWN	HF (num)	HF (bas)
Li $2s$	−7.24917	−7.34097	−7.33519	−7.432727	−7.432710
$2s\uparrow$	−7.26892	−7.35453	−7.34392		
Li_2	−14.548445	−14.737609	−14.725637	−14.871923	−14.871882
Na $3s$	−161.2634	−161.4393	−161.4401	−161.85891	−161.85821
$3s\uparrow$	−161.2805	−161.4511	−161.4476		
Na_2	−322.56976	−322.92632	−322.92742	−323.71728	−323.71583
K $4s$	−598.2062	−598.1817	−598.2006	−599.16475	
$4s\uparrow$	−598.2194	−598.1909	−598.2059		
K_2	−1196.44380	−1196.39918	−1196.43646	−1198.32534	

Total energies evaluated in the one-dimensional calculations for atoms taken from Ref. 24. Li −7.4327269, Na −161.85891, K −599.16479

sets [26] is 0.0015 a.u. corresponding to 0.04 eV. At present there are no accurate LCAO-HF calculations for K_2 rendering a comparison impossible. However, the values determined in this work could be used as benchmarks in the optimization of new basis sets for heavier elements.

By means of the total energies given in Table 1, dissociation energies and different spectroscopic constants have been evaluated and compared with available spectroscopic constants [29] as summarized in Table 2. We notice that the difference earlier observed in total energy between the numerical and basis-dependent HF calculations has disappeared in the spectroscopic constants. In Table 2 results are given to the right from earlier calculations within the local density approximation, LDA, [30, 31] and from different all-electron SCF and valence CI calculations [32] in which intershell correlation effects and an effective core polarization potential, CI-CPP, [32] have been taken into account. Further, results from more recent CI-calculations of Bonačić-Koutecký et al. [27, 28] are given for comparison. The earlier calculations using LDA exchange correlation potentials [30, 31] are in rather good agreement with our calculations using the von Barth–Hedin potential, although with lower numerical accuracy.

An overview of the difference between some of the theoretical results in Table 2 and the corresponding experimental bond lengths and dissociation energies are also presented in Figs. 1 and 2. The dissociation energies evaluated with the von Barth–Hedin [22] and Vosko, Wilk and Nusair potential [23] seem to reasonably well reproduce the experimental values. A very good agreement is obtained between the experimental values [29] and the theoretical ones when intershell correlation effects and the effective core polarization are included [32]. It is surprising that the HF-CI calculations of Bonačić-Koutecký [27, 28] do not reproduce the experimental bond length for Na_2 in a better way than that given in Table 2. If this is due to basis set errors or the neglect of core polarization effects and higher-order terms in the CI expansion is not clear. The question is how this type of deviation will influence the optimization of geometries for clusters bigger than the dimer.

Table 2. Comparison of experimental and theoretical spectroscopic constants for the ground state of Li_2, Na_2 and K_2. The values of D_e given on the second line have been evaluated by means of the total energies for non polarized atomic calculations while those on the third line have been obtained from spin polarized calculations

		Exp.	$X\alpha$	BH	VWN	HF	HF (bas)	LSD	LSD LMTO	CI	CI + CPP	HF-CI
		Ref. [29]	This work				[25]	[30]	[31]	[32]	[32]	[27, 28]
Li_2	r_e (a.u.)	5.051	5.223	5.115	5.119	5.260	5.262	5.12	5.13	5.091	5.044	5.098
	D_e (eV)	1.04	1.356	1.506	1.496	0.176	0.176			1.036	1.048	1.004
	D_e (eV)	1.04	0.287	0.777	1.028			1.0	0.83			
	ω_e (cm^{-1})	351.43	317.3	340.4	339.2	338.0	337	330	340	347.6	351.7	348.3
Na_2	r_e (a.u.)	5.818	5.779	5.659	5.667	6.042	6.039	5.67	5.74	6.006	5.832	6.025
	D_e (eV)	0.720	1.163	1.291	1.278	−0.0148	−0.016			0.717	0.735	0.703
	D_e (eV)	0.720	0.244	0.662	0.882			0.9	0.65			
	ω_e (cm^{-1})	159.12	154.84	162.78	162.37	155.14	155	160	160	151.0	158.5	155.3
K_2	r_e (a.u.)	7.380	7.434	7.256	7.267	7.936			7.30	7.843	7.446	
	D_e (eV)	0.514	0.850	0.967	0.955	−0.1153				0.526	0.537	
	D_e (eV)	0.514	0.137	0.477	0.671				0.47			
	ω_e (cm^{-1})	92.021	87.6	94.7	94.1	88.2			90	83.8	91.8	

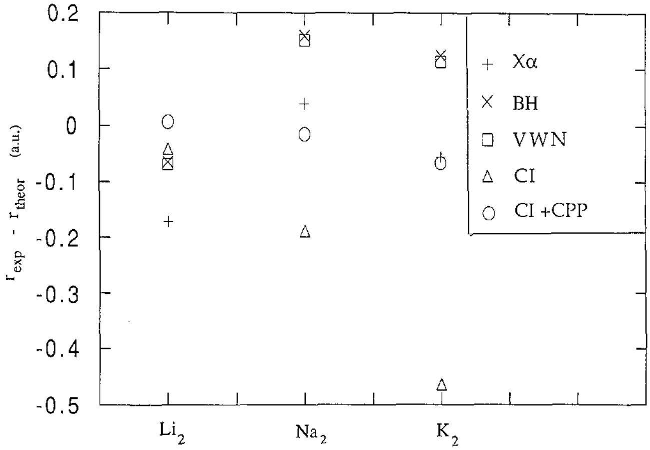

Fig. 1. The difference between the experimental bond lengths and those calculated by means of different exchange correlation potentials, CI and CI + CPP methods

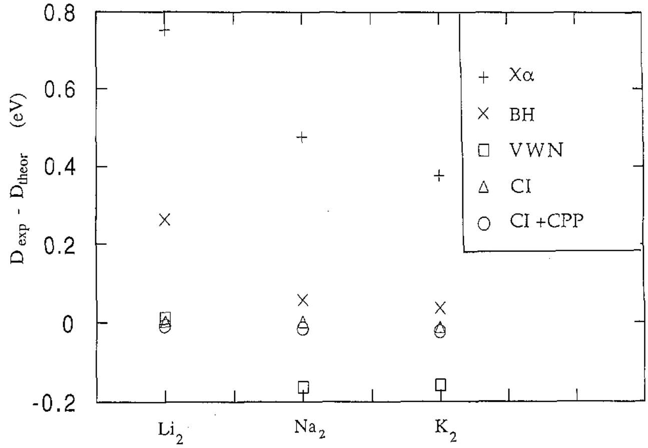

Fig. 2. The difference between the experimental dissociation energies and those calculated by use of different exchange correlation potentials, CI and CI + CPP methods

The total energies and spectroscopic constants evaluated in this work for K_2 can be used as a benchmark in the optimization of basis sets. Further, due to the highly numerically accurate FEM method, work is now in progress to extend the calculations in order to use other exchange correlation potentials such as the one of Ceperley and Alder [33] and also to include gradient corrections as discussed by Becke [34, 35].

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