

# Accurate local density functional calculations with relativistic two-spinor minimax and finite element method for the alkali dimers

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## Abstract

The 2-spinor minimax method combined with the numerical finite element method has proved to be very accurate. One obtains benchmark values in relativistic density functional calculations for diatomic molecules, with the error decreasing systematically with basis set size. In particular, the relativistic contamination errors and the variational collapse, which may occur in the relativistic 4-spinor calculations, are avoided in the 2-spinor minimax formulation of the Dirac equation by exact projection against the negative continuum. In the present work, we investigate the relativistic and nonrelativistic local-density functionals on alkali dimers (Li<sub>2</sub> through Fr<sub>2</sub>), presenting accurate results in the sense that we have an optimized error control. We show that our results have minimal solution errors and report the most accurate values obtained for the respective functional, thus exhibiting the correct behaviour of these functionals and corresponding trends with increasing the atomic charge  $Z$ . In comparison with experiment the alkali dimers exhibit different behaviour than the dimers of group 11, the noble metal group including roentgenium (Rg,  $Z = 111$ ), which were investigated in our previous papers. This is a clear indication that the correlation functional is important for the proper description of alkali dimers.

## 1. Introduction

The alkali dimers have recently attracted increased attention both theoretically and experimentally because of their importance in the formation of cold molecules [1–6]. The chemical properties are experimentally well known up to Cs<sub>2</sub> [7–10]. Non-relativistic theoretical investigations for the lighter molecules Li<sub>2</sub>, Na<sub>2</sub> and K<sub>2</sub> have been performed in an *ab initio* framework [11–13] and using density functional theory (DFT) [14–19]. Relativistic investigations in an *ab initio* framework [20, 21] and, more recently, also in the DFT framework [22] have also been reported.

The 2-spinor minimax method [23–26] combined with the numerical finite element method (FEM) has proved to be very successful. Exploiting extrapolation and counterpoise

techniques, one obtains accurate DFT results with a minimal solution error for diatomic molecules. In the present work, we investigate the non-relativistic and relativistic local density functional approximations, NLDA and RLDA, respectively, and the (Dirac–Hartree–Fock–) Slater approximation DHFS (X<sub>α</sub>–DHFS, with  $\alpha = 0.7$ ). The results allow for detailed and definitive statements on the behaviour of the functionals investigated. Like in our previous papers [25, 26] on the dimers of group 11, we study the trends with increasing nuclear charge,  $Z$ . In addition, we compare the results obtained for the alkali dimers with the results for the dimers of group 11 [26] in order to show the differences and the similarities in the behaviour of these different types of systems.

To date the NLDA values for K<sub>2</sub>–Fr<sub>2</sub> using pseudopotential (PP) techniques [22] are, to our knowledge,

the most accurate relativistic DFT values in the literature. In section 4, it will be shown that our results are very accurate as far as the technical solution error of the underlying computational problem concerned, and we compare them to the PP result of [22]. For the lighter dimers  $\text{Li}_2$ ,  $\text{Na}_2$  and  $\text{K}_2$  we present relativistic as well as non-relativistic values, the latter in order to compare with the non-relativistic values found in the literature. In this way differences to the literature values and the relativistic effects on the bond energies (binding energy) and bond lengths for these light molecules can easily be seen.

There is a large number of publications concerning alkali dimers, and it is not the purpose of the present work to give a complete comparison of different methods. Rather we will focus on DFT calculations and will quote literature DFT values as far as they are known to us. The comparison to experimental results allows for an analysis of the errors associated with (relativistic) LDA-type functionals. It will be shown that it is important to obtain highly accurate values that properly minimize the total energy in order to recover the correct behaviour of the functionals considered for different types of quantum-mechanical systems and to make reasonable conclusions about open questions.

## 2. Method

The 2-spinor fully relativistic FEM approach to the two-centre Coulomb problem in the weak formulation is numerically much better behaved than the 4-spinor form [24]. One finds some desired features and generally much better results in the former approach: in particular the total energy converges from above with increasing grid size (higher accuracy by finer subdivisions) and does not show the typical convergence from below or oscillatory convergence of the 4-spinor Dirac formulation. The errors in the calculations stem solely from the incompleteness of the basis (grid point number), thus the error weighting is similar to that of the non-relativistic Schrödinger equation [24, 27]. The one-particle Dirac equation (matrix form) is

$$\begin{pmatrix} V + mc^2 & \hat{L}^\dagger \\ \hat{L} & V - mc^2 \end{pmatrix} \begin{pmatrix} \phi_i^+ \\ \phi_i^- \end{pmatrix} = \lambda_i \begin{pmatrix} \phi_i^+ \\ \phi_i^- \end{pmatrix} \quad (1)$$

which can be decomposed into

$$\hat{L}^\dagger \phi_i^- = (\lambda_i - mc^2 - V) \phi_i^+ = (\varepsilon_i - V) \phi_i^+, \quad (2)$$

$$\hat{L} \phi_i^+ = (\lambda_i + mc^2 - V) \phi_i^- = (\varepsilon_i + 2mc^2 - V) \phi_i^-, \quad (3)$$

where  $\hat{L} = -i\mathbf{c}\hbar\boldsymbol{\sigma} \cdot \nabla$  and  $c$  and  $\hbar$  are the speed of light and Planck's constant, respectively.  $\hat{\boldsymbol{\sigma}} = \sum_{k=1}^3 \sigma_k \mathbf{e}_k$ ,  $\sigma_k$  are the Pauli matrices. One notices that we introduced both  $\hat{L}$  and  $\hat{L}^\dagger$  (the adjoint operator), because unfortunately one may convince oneself that the momentum operator  $\hat{\mathbf{p}} = \frac{\hbar}{i}\nabla$  is non-Hermitian in the space of finite element functions, indeed the unhermicity depends on the approximation order of the finite element functions, which is of the same order of the total solution error  $\sim \frac{1}{N^p}$ , where  $p$  is the FEM order and  $N$  is the grid points number, i.e.  $\hat{L}$  is Hermitian in a complete basis. For high-order FEM approximation (and large grid points number

$N$ ) this error is too small and is reduced in addition by the extrapolation technique we use in our calculations. It has been proved [23] (and the references therein) that the minimax eigenvalue corresponds to the relativistic eigenvalue of the one-particle Dirac equation  $\lambda_i$ . In equations (2) and (3) we introduced  $\varepsilon_i = \lambda_i - mc^2$ , which shifts the eigenenergies to align the relativistic and non-relativistic energy scales. The large and small components are denoted  $\phi_i^+$  and  $\phi_i^-$  respectively.  $V = V_H + V_{xc} + V_k$  is the total potential,  $V_H$  is the Hartree potential,  $V_{xc}$  is the exchange correlation potential, and  $V_k(\mathbf{r}) = -\sum_{k=1}^2 \frac{Z_k}{|\mathbf{r}-\mathbf{R}_k|}$  the nuclear potential.  $Z_k$  and  $\mathbf{R}_k$  are the charges and the positions of the nuclei, respectively.

For two-centre systems one has axial symmetry and favourably uses prolate spheroidal coordinates  $\xi, \eta, \varphi$  [28–30]. They are given by the transformations:

$$\begin{aligned} x &= \frac{R}{2} \cdot u(\xi, \eta) \cos(\varphi), & y &= \frac{R}{2} u(\xi, \eta) \sin(\varphi), \\ z &= \frac{R}{2} \xi \cdot \eta, & \text{where } u(\xi, \eta) &= \sqrt{(\xi^2 - 1)(1 - \eta^2)} \end{aligned} \quad (4)$$

where  $R$  is the internuclear distance. The Coulomb singularity of point nuclei causes a singular behaviour of the relativistic solutions at the nuclei of the form  $r_i^{-1+\gamma_{l,k}}$  [29, 30], which is well known from atomic calculations, where  $\gamma_{l,k} = \sqrt{\kappa^2 - \left(\frac{Z_l}{c}\right)^2}$ ,  $|\kappa| = |j_z| + \frac{1}{2}$ ,  $l = 1, 2$  (for the two centre in the diatomic molecules). Thus further singular (one-dimensional) coordinate transformations  $\xi(s), \eta(t)$  are used [27]

$$\begin{aligned} \xi &= 1 + c_1 \sinh^\nu(s/2) + c_2 \sinh^{(\nu+2)}(s/2) \dots, \\ \eta &= 1 - c_1 \sin^\nu(t/2) + c_2 \sin^{(\nu+2)}(t/2) \dots, \\ 0 &\leq s < \infty & 0 &\leq t \leq \pi \\ &\text{for } \nu = 2, 4, 6, 8, 10, \text{ with } c_i = 0 \text{ for } i > \frac{\nu}{2}. \end{aligned} \quad (5)$$

The extension of the domain is  $s = S_{\max}$  [24, 25] (see section 3). It has been shown that  $\nu = 4$  (where  $c_1 = 6$ ,  $c_2 = 4$ ) is an optimal value for the 2-spinor minimax calculations [24]. Because of axial symmetry, the angular coordinate  $\varphi$  is treated analytically,

$$\begin{aligned} \psi^T &= (\phi^{+T}, \phi^{-T}) \\ \phi^{+T} &= (\phi^1(s, t) \cdot e^{i(j_z-1/2)\varphi}, \phi^2(s, t) \cdot e^{i(j_z+1/2)\varphi}), \end{aligned} \quad (6)$$

where  $T$  denotes the transpose vector and  $j_z$  is the projection of the total angular momentum to the internuclear axis, the  $z$ -axis. the lower component  $\phi^-$  is obtained from the upper  $\phi^+$  by the relation in equation (3).

In the weak formulation one solves equation (3) for the small component  $\phi_i^-$ , and inserts it into equation (2), multiplies from the left with  $\langle \phi^+ |$  and finally obtains the minimax functional [25]

$$F[\phi_i^+] = \int \frac{\frac{1}{c^2} \|\hat{L}\phi_i^+\|^2}{2m + (\varepsilon_i - V)/c^2} d^3\mathbf{r} - \int (\varepsilon_i - V) \|\phi_i^+\|^2 d^3\mathbf{r}, \quad (7)$$

which has to be minimized by variation with respect to the large component of one-particle wavefunction,  $\phi_i^+$ , with open or closed boundary conditions at a finite boundary. We use an open boundary in our calculations. This is justified for

the piecewise defined FEM functions and by sufficient region extension  $S_{\max}$  [26]. The use of open or closed boundary condition does not influence the accuracy. This has been proved in test calculations for the non-relativistic approach (i.e.  $c \rightarrow \infty$ ), by comparison with a multi-grid code used in our group [31], in which closed boundary conditions are used. The difference between the two results is negligible.

The total potential  $V$  is kept fixed for the minimization of equation (7) in every iteration step of the self-consistent-field (SCF) procedure [26]. The density-dependent part of  $V$ , the Hartree–Coulomb direct and the exchange correlation potentials  $V_H, V_{xc}$  respectively, are then updated with the solutions of equation (7) for the next SCF-step. The potential  $V_{xc}$  we use in the present work for the NLDA is the standard non-relativistic LDA for exchange combined with Vosko, Wilk and Nusair (VWN5) [32] correlation. Accordingly, the RLDA is the relativistic LDA approximation combined with the relativistic extension of VWN [33–36]. Variation of equation (7) with fixed  $V$  with respect to the coefficients of the (unknown) FEM shape functions gives a matrix equation of the form

$$\mathbf{H}(\varepsilon_i) \mathbf{f}_i^+ = \varepsilon_i \mathbf{f}_i^+ \quad (8)$$

where  $\mathbf{f}_i^+$  is the coefficient vector of the  $\phi_i^+$  FEM-approximation. Equation (8) is solved iteratively to obtain the relativistic one-particle eigenvalues  $\varepsilon_i$  and the two large components  $\phi_i^+$  of the relativistic one-particle wavefunction  $\psi_i$ . We note that the dependence of  $\mathbf{H}(\varepsilon_i)$  on  $\varepsilon_i$  can be handled by series expansion around an arbitrary but fixed values  $\varepsilon_0$  [23], so that much fewer matrices need to be updated in order to obtain all eigenvalues in every SCF-iteration [25]. One calculates  $\phi_i^-$  via equation (3), but now one has to normalize the total spinor to unity

$$\langle \psi_i | \psi_i \rangle = \langle \phi_i^+ | \phi_i^+ \rangle + \langle \phi_i^- | \phi_i^- \rangle = 1$$

in order to obtain the density and the potentials  $V_H, V_{xc}$ . The total energy of the system is given by

$$E_{\text{tot}} = \sum_{i=1}^N \varepsilon_i - \frac{1}{2} \int_{S_{\max}} \rho(\mathbf{r}) V_H(\mathbf{r}) \, d\mathbf{r}^3 + \int_{S_{\max}} \times (\varepsilon_{xc}[\rho(\mathbf{r})] - V_{xc}(\rho(\mathbf{r}))) \rho(\mathbf{r}) \, d\mathbf{r}^3 + E_{\text{nuc}}, \quad (9)$$

where  $\varepsilon_{xc}$  is the exchange-correlation energy density,  $V_{xc} = \frac{\partial}{\partial \rho} \varepsilon_{xc}[\rho]$  is the exchange-correlation potential,  $V_H$  is the Hartree potential and  $E_{\text{nuc}}$  is the internuclear repulsion energy. This energy expression is particularly well suited for the SCF-iteration process, if the same  $V_H$  and  $V_{xc}$  are used to compute the current  $\varepsilon_i$  and  $\psi_i$ ,  $i = 1, \dots, N$  by solving the one-particle equation via the minimax method equations (7) and (8). In the iterative SCF-procedure,  $E_{\text{tot}}$  has only errors of order  $(\delta\rho)^2$  [37]. In equation (9),  $E_{\text{tot}} = E_{\text{tot}}[\rho]$  is a functional of the total density  $\rho = \sum_{i=1}^N n_{\text{occ},i} \|\psi_i\|^2$ ,  $n_{\text{occ},i}$  are the occupation numbers of the  $i$ th orbital, and  $\rho$  is obtained from the 4-spinor component wavefunctions  $\psi_i$ , even though from equations (7) and (8) only the (2-spinor) large  $\phi_i^+$  component is calculated. Important is the convergence from above, because this prevents an otherwise uncontrolled pick-up of positronic (negative continuum) contributions to the solutions of the Dirac equations: the stationarity principle of the Dirac

formulation is replaced by a minimax principle in the space of the electronic states. This is a fundamental advantage of the 2-spinor relativistic formulation which is reflected by an improved numerical behaviour.

### 3. Computational details

All values of the present work are obtained using point-like nuclei and seventh-order FEM Lagrange polynomials with a coordinate transformation of type  $\nu = 4$ , like in our previous papers and the speed of light is set to 137.035 9895 a.u. The FEM values for atoms are calculated for spin-unpolarized atoms and then the polarization effect is added, which is taken from atomic calculations using an atomic code [39]. The extension of the region is  $S_{\max} = 35$  a.u. which is larger than in our previous work [25, 26] due to the weak bonding (long bond length) of the alkali dimers. For  $\text{Fr}_2$  the calculations were performed with 9801 grid points, for the other dimers smaller grids were sufficient. In our calculations we use a counterpoise and extrapolation technique (geometrical over the SCF-iteration number and rational over the number of grid points [24–27]). We use point-like nuclei for all calculations. This is justified, first the weak singularity of the wavefunction in the vicinity of the nuclei is regularized, as mentioned above, using the coordinate transformations in equation (5) and investigated in previous paper [24, 27]. Second, we compare results of the same model, and it is known that the effect of finite-nucleus models on chemical properties is negligible. For instance, for the noble metal dimers [38], where the authors use a linear combination of Gaussian-type orbitals DFT method, the investigation of the finite-nucleus effect showed that there is no effect on the binding energies, bond lengths and vibrational frequencies for  $\text{Cu}_2$  and  $\text{Ag}_2$  dimers. For  $\text{Au}_2$  it is zero on the vibrational frequency, the bond length increased by 0.002 a.u., and the binding energy decreased by  $-0.001$  eV. Due to the weak binding and large bond length compared to the noble metal dimers, one expect that these effects will be below (i.e. almost zero) for the alkali dimers  $\text{Li}_2$ – $\text{Cs}_2$  and negligibly small for the  $\text{Fr}_2$  dimer. In particular, the differences between the results obtained with extended and point nuclei do not affect our conclusions concerning the properties of local exchange-correlation functionals.

### 4. Results and discussion

Dissociation energies  $D_e$ , bond lengths  $R_e$  and vibrational frequencies  $\omega_e$ , obtained for the dimers  $\text{Li}_2$  through  $\text{Fr}_2$  are listed in tables 1–3. The comparison with literature values in table 1 shows a good agreement with the pseudopotential results of [22] for NLDA. The values of [22] are 9, 13, 14 and 8 meV larger in the energy than our highly accurate 2-spinor values for  $\text{K}_2$  throughout  $\text{Fr}_2$ , respectively. We note that according to [22] the accuracy in the pseudopotential fitting procedure was between 10 and 20 meV, whereas we have a better numerical error control and the accuracy in our 2-spinor values is within 1 meV (as extracted from the convergence behaviour with increasing grid points). The differences between the NLDA values of [22] and our 2-spinor minimax

**Table 1.** Ground-state ( $X\Sigma_g^+$ ) bond energies  $D_e$  [eV] of alkali dimers for NLDA, RLDA and Slater functional approximation.

Method	Reference	Li <sub>2</sub>	Na <sub>2</sub>	K <sub>2</sub>	Rb <sub>2</sub>	Cs <sub>2</sub>	Fr <sub>2</sub>
Slater (RL)	[pw]	0.289	0.244	0.141	0.139	0.121	0.181
RLDA (RL)	[pw]	1.027	0.88	0.67	0.631	0.576	0.606
NLDA (RL)	[pw]	1.027	0.88	0.67	0.631	0.577	0.609
NLDA <sup>a</sup> (RL)	[22]	–	–	0.679	0.644	0.591	0.617
NLDA (Non-RL)	[pw]	1.027	0.878	0.666	–	–	–
NLDA <sup>b</sup> (Non-RL)	[19]	1.030	0.883	–	–	–	–
NLDA <sup>c</sup> (Non-RL)	[18]	1.02	0.79	0.59	–	–	–
NLDA <sup>d</sup> (Non-RL)	[16]	1.0	0.9	–	–	–	–
NLDA <sup>e</sup> (Non-RL)	[15]	0.83	0.65	0.49	–	–	–
NLDA <sup>f</sup> (Non-RL)	[14]	0.83	0.65	0.47	–	–	–
LDAX <sup>g</sup> (Non-RL)	[17]	–	0.95	0.67	–	–	–
RPP-PW91 <sup>a</sup> (RL)	[22]	–	–	0.601	0.544	0.508	0.503
PP-PW86 <sup>b</sup> (Non-RL)	[41]	0.96	0.83	0.60	–	–	–
RPP-B3LYP <sup>a</sup> (RL)	[22]	–	–	0.502	0.448	0.388	0.391
RPP-CC <sup>i</sup> (RL)	[22]	–	–	0.531	0.465	0.425	0.431
Experiment	[42–44]	1.04	0.756	0.52	0.485	0.452	–

[pw] Present work.

<sup>a</sup> Relativistic pseudopotential.<sup>b</sup> All-electron calculation.<sup>c</sup> Nonlinear augmented plane wave method.<sup>d</sup> Non-relativistic numerical method.<sup>e</sup> Non-relativistic PP-LDA.<sup>f</sup> Non-relativistic *ab initio* LMTO-LDA.<sup>g</sup> Non-relativistic PP, LDAX (exact exchange + LDA correlation).<sup>h</sup> LCAOGTO-DFT.<sup>i</sup> RPP with coupled cluster.**Table 2.** Ground-state ( $X\Sigma_g^+$ ) bond length  $R_e$  (a.u.) of alkali dimers for NLDA, RLDA and Slater functionals approximation.

Method	Reference	Li <sub>2</sub>	Na <sub>2</sub>	K <sub>2</sub>	Rb <sub>2</sub>	Cs <sub>2</sub>	Fr <sub>2</sub>
Slater (RL)	[pw]	5.223	5.778	7.403	7.893	8.741	8.565
RLDA (RL)	[pw]	5.119	5.663	7.237	7.722	8.548	8.395
NLDA (RL)	[pw]	5.119	5.663	7.237	7.715	8.537	8.384
NLDA <sup>a</sup> (RL)	[22]	–	–	7.153	7.659	8.489	8.40
NLDA (Non-RL)	[pw]	5.119	5.672	7.267	–	–	–
NLDA <sup>b</sup> (Non-RL)	[19]	5.118	5.673	–	–	–	–
NLDA <sup>c</sup> (Non-RL)	[18]	5.20	5.96	7.43	–	–	–
NLDA <sup>d</sup> (Non-RL)	[16]	5.05	5.67	–	–	–	–
NLDA <sup>e</sup> (Non-RL)	[15]	5.15	5.75	7.15	–	–	–
NLDA <sup>f</sup> (Non-RL)	[14]	5.13	5.74	7.3	–	–	–
LDAX <sup>g</sup> (Non-RL)	[17]	–	5.52	7.068	–	–	–
RPP-PW91 <sup>a</sup> (RL)	[22]	–	–	7.474	8.028	8.906	8.825
RPP-B3LYP <sup>a</sup> (RL)	[22]	–	–	7.43	8.014	8.921	8.527
RPP-CC <sup>i</sup> (RL)	[22]	–	–	7.408	7.907	8.770	8.679
Experiment	[42–44]	5.046	5.67	7.415	7.899	8.78	–

[pw] Present work.

<sup>a–g,i</sup> See table 1.

values can alternatively be interpreted to be due to the well-known interplay between different error sources in relativistic methods, namely basis limitation leading to shallower energy values. On the other hand, in 4-spinor methods the contamination error leads to lower energy values. In addition, the (relativistic) pseudopotential methods according to the results shown in the literature show values below our minimax FEM values, most likely due to the error in the fitting procedure (see also the comparison to [40] given in [26] for group 11). For completeness, we also account for the contributions due to spin-polarization in the dissociation energies in table 1, namely two times the atomic spin-polarization effects

–0.2289, –0.2333, –0.2686, –0.2972, –0.4070, –0.477 in eV for Fr through Li, respectively, which have been added to the unpolarized atomic FEM ground state energies. The values corresponding to [14, 15, 16, 17, 18, 19, 41] for Li<sub>2</sub>–K<sub>2</sub> in the tables 1–3 are non-relativistic calculations. There is good agreement with [19] for Li<sub>2</sub> and Na<sub>2</sub> with our non-relativistic values in all properties  $D_e$ ,  $R_e$  and  $\omega_e$ . The other literature values are to some extent in good agreement with our values but, in detail, one finds some differences even for these small and light molecules. As to be expected, (cf table 1), relativistic effects on the bonding of Li<sub>2</sub> and Na<sub>2</sub> can be neglected.

**Table 3.** Ground-state ( $X\Sigma_g^+$ ) vibrational frequencies  $\omega_e$  ( $\text{cm}^{-1}$ ) of alkali dimers for NLDA, RLDA and Slater functionals approximation.

Method	Reference	Li <sub>2</sub>	Na <sub>2</sub>	K <sub>2</sub>	Rb <sub>2</sub>	Cs <sub>2</sub>	Fr <sub>2</sub>
Slater (RL)	[pw]	316.5	153.6	87.4	55.2	39.8	32.6
RLDA (RL)	[pw]	337	163	94.4	59.5	43.3	35
NLDA (RL)	[pw]	337	163	94.4	59.5	43.4	35.6
NLDA <sup>a</sup> (RL)	[22]	–	–	97.9	62	44.3	36
NLDA (Non-RL)	[pw]	337	163	94	–	–	–
NLDA <sup>b</sup> (Non-RL)	[19]	338	162	–	–	–	–
NLDA <sup>c</sup> (Non-RL)	[18]	322	157	84	–	–	–
NLDA <sup>d</sup> (Non-RL)	[16]	330	160	–	–	–	–
NLDA <sup>e</sup> (Non-RL)	[15]	336	162	97	–	–	–
NLDA <sup>f</sup> (Non-RL)	[14]	340	160	90	–	–	–
LDAX <sup>g</sup> (Non-RL)	[17]	–	184	92	–	–	–
RPP-PW91 <sup>a</sup> (RL)	[22]	–	–	90.2	56.7	41	32.2
RPP-B3LYP <sup>a</sup> (RL)	[22]	–	–	90.8	56.7	40.5	32
RPP-CC <sup>i</sup> (RL)	[22]	–	–	92.3	58.3	42.4	33.5
Experiment	[42]–[45]	340	159.2	92	57.8	42	–

[pw] Present work.

<sup>a–g,i</sup> See table 1.

Concerning the difference between the Slater approximation and the LDA, we see that the former strongly underestimates the dissociation energy, while the LDA overestimates it. The LDA behaves similarly for alkali dimers and the dimers of the group 11, whereas the Slater approximation describes the dimers of the group 11 considerably better than the alkali dimers. This can be understood following an analysis of the exchange-correlation hole in [46, 47] (for the H<sub>2</sub> molecule) that: in the alkali dimers, the exchange-correlation hole is delocalized in the binding region and the electronic density is quite diffuse, leading to an underestimation of the electron-nuclear attraction, whereas in the dimers of the group 11 the exchange-correlation hole is more localized in the binding region where the electronic density is large and less diffuse (which explains the success of the Slater approximation to describe these types of molecules). The Slater approximation overestimates the dissociation energies of the noble metal dimers by only about 10–15% (absolute 0.2–0.37 eV for Cu<sub>2</sub> through Au<sub>2</sub>), but underestimates the dissociation energy by about 70% for the alkali dimers (absolute 0.38–0.33 eV K<sub>2</sub> through Cs<sub>2</sub>). The LDA overestimates the dissociation energy in both cases (alkali dimers and group 11 dimers) by about 30% (absolute about 0.7 eV for the dimers Cu<sub>2</sub> through Au<sub>2</sub>, and about 0.15–0.13 eV for alkali dimers K<sub>2</sub> through Cs<sub>2</sub>). One may conclude that the Slater approximation has a more local character than the LDA, even though both use only the local density. It is the different functional dependence (the VWN-correlation and  $X_\alpha$  parameter) on the density which contains (in an average way) information about the delocalization of the density. In other words, in the NLDA the correlation contributions are represented—on average—similarly for both, the dimers of group 1 (delocalized density) and the dimers of group 11 (localized or less diffusive density). While the correlation contributions are not represented sufficiently in the Slater approximation, one obtains better results for systems like the group 11, in which the density is larger in the bonding region and less diffuse, which means that the long range correlation contributions are small.

From tables 1 to 3 we see the well-known fact that the alkali dimers have small dissociation energies, long bond lengths and small vibrational frequencies. Moreover, there is a trend towards smaller  $D_e$  and longer  $R_e$  up to Cs<sub>2</sub> while in Fr<sub>2</sub> the binding becomes stronger and the bond length shorter due to the well-known relativistic contraction effect. On the other hand, the vibrational frequency of Fr<sub>2</sub> remains smaller than that of the other dimers in the group. However taking the increase of the mass in account, one finds that the ratio of the force constants is approximately constant.  $\sqrt{\frac{k_i}{k_{i+1}}} = \frac{\omega_i}{\omega_{i+1}} \cdot \sqrt{\frac{m_i}{m_{i+1}}} \approx 1.036, 1.05$  for the sequence Rb<sub>2</sub>, Cs<sub>2</sub> and Fr<sub>2</sub>, respectively. The corresponding masses of the atoms, used in our Morse-fitting procedure, are 6.941, 22.99, 39.098, 85.468, 132.91, 223.02 for Li through Fr, respectively. Concerning the bond lengths given in table 2, we see again that the correction resulting from the relativistic nature of the RLDA is relatively small. Compared to the literature values for the NLDA, the deviations from the values of [22] amount to  $\Delta R_e$  (NLDA<sub>FEM</sub> - NLDA<sub>PP</sub>) = 0.084, 0.056, 0.047, –0.0159 for K<sub>2</sub> through Fr<sub>2</sub>, respectively. The differences between the two methods become smaller towards larger  $Z$ . Compared to experiment, the Slater values are better than those from NLDA and RLDA. The bond lengths for the three functionals are shorter than experimental ones, a typical behaviour of local density functionals. Moreover, the error becomes larger towards large  $Z$  and amounts to +0.07, –0.01, –0.18, –0.184, –0.23 in a.u., for Li<sub>2</sub> through Cs<sub>2</sub>, respectively). This is unlike what we have seen for the dimers of the group 11 [26].

In table 3, we compare the vibrational frequencies  $\omega_e$  for the same systems with literature and experimental values. As discussed in [26],  $\omega_e$  is sensitive to the accuracy of the bond energy values at different internuclear distances  $D(R)$ , which we obtain from Morse fittings of several values  $D(R)$ . In our fitting procedure we have ensured that our data ( $D(R)$ ) have an accuracy of  $10^{-6}$  a.u. in the case of the largest grid and take a reasonably small region around the equilibrium bond length (roughly  $R_e \pm 0.5$  a.u.) with 8–12 points, chosen

equidistantly for the fitting procedure. We note that a Morse-potential fitting for highly accurate data must be stable with only a few points, which we indeed observed in our fitting. Compared to experiment, the  $\omega_e$  values are reasonable and have about the same quality for the three functionals and the differences between our values and the values for [22] of the NLDA functional are small.

## 5. Conclusion

We have presented highly accurate 2-spinor minimax FEM results for the alkali dimers, using different local density functional models. Our calculations are highly accurate in the sense that we have excellent control over the solution error. We have looked at three models, the Slater  $X_\alpha$  approximation, the non-relativistic and the relativistic local density approximations NLDA and RLDA. However, further improvement will be sought by going beyond the LDA. In [26] we argued that a similar behaviour to the coinage dimers is expected to hold for other molecules, but in view of the present work, this expectation cannot be confirmed. Because of the weak binding in the alkali dimers the core-valence correlation and the long-range correlation become dominant. Therefore, it may not be surprising that the coupled cluster calculations with pseudopotential (CCRPP) [22], which treat the molecular exchange correlations on a high level comes closest to experimental data. From tables 1–3, one sees trends with increasing  $Z$ . It turns out that the Slater approximation fails to give reasonable  $D_e$  for all dimers considered here, most likely due to insufficient correlation contributions. For the vibrational frequencies all three local approximations DHFS, NLDA and RLDA have a similar quality, whereas for  $R_e$  the DHFS approximation gives better results compared to experimental values. RLDA behaves better than NLDA but the correction is very small even for  $\text{Fr}_2$ . Unfortunately no experimental values for  $\text{Fr}_2$  are available, because bond energies (table 1) in particular show an interesting interplay between relativity and exchange correlation effects. In comparison to the literature the differences are relatively small for the heavier dimers of  $\text{Rb}_2$ – $\text{Fr}_2$ . For the lighter dimers  $\text{Li}_2$ – $\text{K}_2$  more non-relativistic values exist in the literature, where some of them are in good agreement with our FEM values. It would be interesting to investigate the behaviour of diatomic compounds of the alkali metals and elements of the group 11, like alkali aurids, which are compounds of the group 1 and gold, or the compounds of elements of group 1 and Rg. The alkali aurids [48, 49] and the alkali-roentgenium diatomic molecules should show behaviour closer to that of the dimers of the group 11 for the three local functionals under consideration.

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