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A Theoretical Benchmark Study of the Spectroscopic Constants of the Very Heavy Rare Gas Dimers

Avijit Shee^a, Stefan Knecht^b and Trond Saue^{*a}

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Spectroscopic constants for the homonuclear dimers of the very heavy rare gases radon (Rn) and eka-radon (Uuo) are reported. A computational protocol using the eXact 2-Component molecular-mean field Hamiltonian has been established based on extensive calculations of the xenon dimer. We find that reliable results require CCSD(T) calculations at the extrapolated basis set limit. In this limit counterpoise corrected results are closer to experimentally derived values than uncorrected ones. Furthermore, in an attempt to reduce the computational cost while retaining very high accuracy, we studied the performance of range-separated density functional theory. Although we observe a somewhat more favorable basis set convergence and reduced importance of connected triples with range-separated methods compared to pure wave function theory, in practice we have to employ the same computational protocol for obtaining converged results. At the Dirac-Coulomb level we find an almost fourfold increase of binding energy when going from the radon to the eka-radon dimer, but the inclusion of spin-other-orbit interaction reduces the dissociation energy of the heaviest dimer by about 40 %.

1 Introduction

Rare gas dimers are bound species because of the dispersion interaction, which is generally characterized as an attractive interaction between the induced dipoles of each monomer. In the framework of wave function theory (WFT), the generation of induced dipoles can only be described by adding excited determinants to the ground state Hartree-Fock (HF) determinant. Therefore, the potential energy curves of those dimers at the HF level is repulsive. Consideration of excited determinants, on the other hand, leads to the possibility of various kinds of interaction, namely, Coulombic attraction or repulsion, induction and dispersion at the same time. Careful treatment of all those interactions requires very sophisticated theoretical approaches. It has been demonstrated by Hobza *et al.*¹ that the inclusion of up-to triple excitations in a Coupled Cluster (CC) expansion and extrapolation to the complete basis set limit (CBS) can provide chemical accuracy (~ 1 kcal/mol) for such systems. The overwhelming cost of CC methods at the CBS limit, though, has encouraged the development of various new theoretical techniques to reach the same accuracy with a much cheaper computational setup.^{2,3}

Density Functional Theory (DFT) is undoubtedly the most-used quantum chemistry method.⁴ However, it is well-known

that standard approximate DFT functionals, with a local *ansatz*, are unable to capture dispersion interaction.^{5,6} In recent years there has been intense development of dispersion corrections within the framework of Kohn-Sham theory, mostly by inclusion of explicit dispersion coefficients (C_6 and higher) and the proper distance dependence.^{7–14} An alternative is provided by range-separated DFT, introduced by Savin,¹⁵ which allows one to graft WFT correlation methods onto DFT without double counting of electron correlation. The resulting long-range WFT – short-range DFT (lrWFT-srDFT) method formally comes with the computational cost of the selected WFT component. However, it has been argued that range-separated methods have a weaker basis set dependence as well as less severe requirements for the size of the correlation space and excitation rank.¹⁶ One of our objectives of the present work is therefore to investigate whether such methods can yield CCSD(T)/CBS-like accuracy for van der Waals dimers at reduced computational cost.

The homonuclear dimers of He, Ne, Ar, Kr and Xe have been studied extensively both theoretically and experimentally by various groups (see Refs. 17–28 and references therein). However, the dimers of the heavier elements in this group, that is, Rn ($Z=86$) and eka-Rn ($Z=118$; ununoctium), have not been studied at all by experiment and very rarely by theory.^{29–32} In passing we should note that the chemical exploration of radon is limited due to its price and radioactivity, and it is mostly known as a health hazard,^{33–35} whereas (possibly) only three single atoms of the isotope ²⁹⁴118 have been synthesized.^{36–38} The half-life of this isotope is 0.89 ms, which is beyond the

^aLaboratoire de Chimie et Physique Quantiques (UMR 5626), CNRS/Université Toulouse III - Paul Sabatier, 118 Route de Narbonne, F-31062 Toulouse cedex, France

^bLaboratory of Physical Chemistry, ETH Zürich, Vladimir-Prelog-Weg 2, 8093 Zürich, Switzerland

*E-mail: trond.sau@irsamc.ups-tlse.fr

limits of present-day techniques for the chemical study of superheavy elements.^{39,40}

Runeberg and Pyykkö²⁹ have reported spectroscopic constants of Rn_2 (and Xe_2) obtained at the CCSD(T) level using relativistic pseudopotentials. Nash, applying a similar computational protocol, have provided corresponding data for Rn_2 and eka-Rn_2 .³⁰ More recently, Kullie and Saue reported spectroscopic constants for the complete series of homoatomic rare gas dimers using MP2-srDFT and the 4-component relativistic Dirac-Coulomb (DC) Hamiltonian.³² For the heaviest dimers there is, however, significant discrepancy between results (as shown in the lower parts of Tables 2 and 3). For instance, for Rn_2 Runeberg and Pyykkö obtains a dissociation energy $D_e = 222.6 \text{ cm}^{-1}$ and estimates $D_e = 276.6 \text{ cm}^{-1}$, which is still far from 323.9 cm^{-1} reported by Kullie and Saue (MP2-srLDA) and from 129.1 cm^{-1} , reported by Nash. Likewise, Kullie and Saue obtain $D_e = 1199.1 \text{ cm}^{-1}$ for eka-Rn_2 , which is more than twice the value 500.1 cm^{-1} reported by Nash. In the present study we therefore carry out 2-component relativistic CCSD(T) as well as CCSD(T)-srLDA calculations in an attempt to provide reference values for the spectroscopic constants of the dimers of the very heavy rare gases and to establish a computational protocol for reliable theoretical studies of the chemistry of the heaviest rare gases. This effort constitutes the very first use of IrCC-srDFT methods with a relativistic Hamiltonian.

Our paper is organized as follows: In Section 2 we discuss our choice of relativistic all-electron Hamiltonian and correlation methods. Computational details are given in Section 3. In Section 4 we present and discuss our results, starting with a calibration study of the xenon dimer. We conclude and provide perspectives in Section 5.

2 Theoretical Considerations

2.1 Choice of Hamiltonian

The selected compounds clearly call for a careful relativistic treatment, including both scalar-relativistic and spin-orbit effects. Starting from the 4-component Dirac Hamiltonian in the molecular field one may add the two-electron Coulomb term, which provides not only the instantaneous two-electron Coulomb interaction, but also two-electron spin-same orbit (SSO) interaction.⁴¹ For very accurate calculations higher-order contributions to the fully relativistic two-electron interaction, notably the spin-other orbit (SOO) interaction, as well as QED corrections may be considered. Formally, WFT-based electron correlation calculations have exactly the same cost using 2- and 4-component relativistic Hamiltonians, to the extent that the latter Hamiltonians are employed within the no-pair approximation (that is, negative-energy orbitals are excluded). This is easily seen from a consideration of the elec-

tronic Hamiltonian in second-quantized form

$$H = E^{HF} + \sum_{p,q} F_p^q \{a_q^\dagger a_p\} + \frac{1}{4} \sum_{p,q,r,s} V_{pq}^{rs} \{a_r^\dagger a_s^\dagger a_q a_p\}, \quad (1)$$

where $\{\}$ denotes normal ordering with respect to the Fermi (HF) vacuum: The number of Fock matrix elements F_p^q and anti-symmetrized two-electron integrals V_{pq}^{rs} will be exactly the same at the 2-component (2c) and 4-component (4c) level. However, the large prefactor of the 4-index transformation at the 4c level, due to the small-component basis functions, may favor the use of a 2c relativistic Hamiltonian, even though the formal scaling of this computational step is generally lower than the correlated calculation itself. An interesting alternative is provided by the eXact 2-Component (X2C) molecular-mean field (mmf) Hamiltonian,⁴² where the converged 4-component Fock operator is subjected to an exact block diagonalization from which the corresponding 2c Fock operator for positive-energy orbitals only is extracted and represented by the large-component basis. The two-electron Coulomb term is thus left untransformed, formally introducing "picture change errors",^{43–45} but the resulting X2C_{mmf}^{DC} Hamiltonian has been shown to provide very close agreement with 4c correlated calculations, at least when only valence electrons are correlated.⁴² It is also possible to include the Gaunt term, and thereby SOO interactions, in a molecular mean-field manner. We denote this Hamiltonian X2C_{mmf}^{DCG} .

In the present study our correlated calculations have been carried out on top of both HF and short-range Kohn-Sham reference functions, as will be described in the following subsections.

2.2 Wave Function Theory

We have considered a range of correlation methods: second-order Møller-Plesset perturbation theory (MP2), coupled-cluster singles-and-doubles (CCSD) and CCSD with approximate triples (CCSD(T)) in the present work. Although MP2 is widely employed to study weak intermolecular interactions, deficiencies have been identified which may lead to a huge overestimation of non-covalent binding energies.^{46,47} In particular, Szabo and Ostlund demonstrated that the MP2 energy of a closed-shell diatomic molecule formed by two closed-shell atoms has the correct long-range R^{-6} behavior

$$\lim_{R_{AB} \rightarrow \infty} E_{AB}^{MP2} = E_A^{MP2} + E_B^{MP2} + \frac{C_6^{AB}}{R_{AB}^6}, \quad (2)$$

but with the C_6^{AB} dispersion coefficient calculated at the uncoupled HF level of theory.⁴⁸ The CCSD method takes into account all intra-atomic correlation contributions up-to singles and doubles amplitudes, but it has been shown that CCSD can significantly underestimate non-covalent binding energies (see

for instance ref. 49,50). In contrast, inclusion of connected triples of inter-atomic type and hence attractive, improves the description vastly. The inclusion of 4th and 5th order of connected triples i.e CCSD(T), is therefore the current reference method for non-covalent interactions.^{51–53}

2.3 Range-separated theory

The first implementation of the lrCC-srDFT method was reported by Goll, Werner and Stoll,¹⁶ who also reported calculated spectroscopic constants of the homoatomic dimers of He, Ne, Ar, Kr and Xe, the latter two rare gas elements described by relativistic effective core potentials. In the present work we report the first implementation and application of the lrCC-srDFT method at the 2c/4c relativistic level. In this section we briefly outline the theory of the lrCC-srDFT method. Further information can be obtained by consulting ref. 16 and references therein.

One starts from a separation of the two-electron Coulomb term V_{ee} into a short-range part V_{ee}^{sr} and its complement V_{ee}^{lr} . The latter is denoted the long-range part, although in practice it is non-zero at *all* interelectronic distances r_{12} . Ideally the separation should be such that the long-range part, to be handled by WFT, carries a maximum of static correlation and a minimum of dynamic correlation as well as providing mathematically tractable two-electron integrals. The most common choice is defined in terms of the error function¹⁵

$$V_{ee}^{lr}(1,2) = \frac{\text{erf}(\mu r_{12})}{r_{12}} \quad (3)$$

where the range-separation parameter μ can take any value between 0 and ∞ ; $\mu = 0$ defines pure Kohn-Sham DFT and $\mu \rightarrow \infty$ corresponds to pure WFT. μ^{-1} has units of length, but one should note that the long-range potential, eqn (3), corresponds to that of a Gaussian charge distribution rather than a hard-sphere model.³² If one therefore wants to associate the range-separation parameter with a radius R around the reference electron, one should choose $\mu^{-1} = R\sqrt{2/5}$ which provides identical root-mean-square radii for the two models.

The energy functional of lrWFT-srDFT theory

$$E[n] = \min_{\Psi_\mu \rightarrow n} \langle \Psi_\mu | T + V_{ee}^{lr} | \Psi_\mu \rangle + E_{Hxc}^{sr}[n] + \int n(1)v_{eN}(1)d1, \quad (4)$$

to be minimized with respect to the (number) density n , is obtained through a generalized adiabatic connection⁵⁴ to a fictitious system, defined by μ , with long-range interaction only. The wave equation of the fictitious system is

$$\hat{H}_\mu \Psi_\mu = E_\mu \Psi_\mu; \quad \hat{H}_\mu = T + V_{eff}^\mu + V_{ee}^{lr}, \quad (5)$$

where we impose that the local effective potential

$$V_{eff}^\mu = v_{eN} + V_{Hxc}^{sr}; \quad V_{Hxc}^{sr}(1) = \frac{\delta E_{Hxc}^{sr}}{\delta n(1)} \quad (6)$$

affords the same electron density as the real interacting system. Analogous to conventional Kohn-Sham theory, the exact form of the short-range Hartree, exchange and correlation (Hxc) energy functional E_{Hxc}^{sr} is not known, but since it is restricted to the short-range part of the total electron interaction (as well as the coupling to the long-range part), one may hope that local approximations may be even more effective than in conventional DFT.

A fundamental difference between conventional Kohn-Sham theory and lrWFT-srDFT theory is that the fictitious system of the latter is interacting so that its wave function Ψ_μ can not be expressed in terms of a single Slater determinant. The approximate methods of WFT are therefore invoked to solve eqn (5). Calculations generally starts with a single-determinant *ansatz* HF-srDFT,⁵⁵ corresponding to a Kohn-Sham calculation with a range-separated hybrid (RSH),⁵⁶ which provides an orbital set for more elaborate correlation calculations. It also defines a partitioning of the Hamiltonian

$$H_\mu = H_{\mu;0} + W_\mu \quad (7)$$

where the zeroth-order Fock-like Hamiltonian

$$H_{\mu;0} = T + V_{eN} + J^{lr}[n_0] + V_{Hxc}^{sr}[n_0] \quad (8)$$

is defined in terms of the zeroth-order density n_0 . The perturbation

$$W_\mu = \underbrace{V_{ee}^{lr} - J^{lr}[n_0]}_{\text{lr fluctuation potential}} + \underbrace{V_{Hxc}^{sr}[n] - V_{Hxc}^{sr}[n_0]}_{\text{self consistency correction}} \quad (9)$$

contains a long-range fluctuation potential as well as a short-range self-consistency correction, the latter reflecting the change of the density from the initial HF-srDFT calculation to the final correlated level. The self-consistency correction does not enter the lrMP2-srDFT energy expression,^{57,58} but formally enters lrCC-srDFT theory. However, studies by Goll *et al.*¹⁶ indicate that the effect of the density update is quite small, and it will be ignored in the present work.

2.4 Basis set extrapolation

The accuracy of correlation methods also entails that we have to cancel out other sources of error such as the basis set incompleteness. For pure WFT correlation methods, the two-point extrapolation scheme advocated by Helgaker *et al.*^{59,60} provides a convenient means for calculating the energy at the extrapolated basis set limit:

$$E_\infty = E_X^{SCF} + \frac{X^3 E_X^{corr} - (X-1)^3 E_{(X-1)}^{corr}}{X^3 - (X-1)^3}. \quad (10)$$

Here X is the cardinal number of the correlation-consistent basis set.

For range-separated methods the situation is less clear. Very recently, Franck *et al.* have proposed a three-point scheme based on an exponential formula,⁶¹ but we feel that further study is required to settle this issue and have not applied the proposed scheme in the present work.

3 Computational Details

We performed all calculations with a development version of the DIRAC-13 quantum chemistry package.⁶² Unless otherwise stated all calculations are based on the 2-component relativistic $X2C_{mmf}^{DC}$ Hamiltonian based on the 4-component Dirac-Coulomb Hamiltonian.⁴² A Gaussian nuclear model has been chosen for the nuclei.⁶³ We applied uncontracted large-component basis sets of Dyal-type^{64,65} including core-correlating and diffuse functions up to quadruple- ζ quality (highest available set). The corresponding small component basis set is generated using the restricted kinetic balance condition.

In our range-separated DFT studies a short-range LDA exchange-correlation functional was used for all cases.^{66,67} We have chosen a system-independent fixed value $0.4 a_0^{-1}$ as our range separation parameter (μ), following the suggestion by Fromager *et al.*,⁶⁸

Spectroscopic constants have been derived by a least square fit of the potential energy curve (PEC) to a polynomial using the TWOFIT utility program available in DIRAC. Throughout this study, we have chosen nine grid points and fitted them against an eighth-degree polynomial. The grid has been generated inside the classical turning points of the PEC. For Xe_2 the grid was generated around the experimental equilibrium bond length, whereas for the heavier dimers we used the best estimate from previous studies.

4 Results and Discussions

4.1 Calibration Study

We first carried out a calibration study of the xenon dimer with the goal to define a suitable computational protocol in terms of (i) correlation method, (ii) number of active occupied orbitals and (iii) basis set level. We consider the convergence of spectroscopic constants with respect to these parameters rather than their agreement with experimental values in order to avoid getting the right result for the wrong reason. Throughout the calibration study, we compared results of two augmented correlation-consistent basis sets for relativistic calculations provided with the DIRAC package, namely dyall.acv3z (TZ) and dyall.acv4z (QZ).⁶⁴ Subsequently, we extrapolated the pure WFT data to the complete basis set limit using eqn(10). The basis set superposition error (BSSE)

was addressed by means of the counterpoise correction approach.⁶⁹ MP2, CCSD and CCSD(T) have been considered for the correlation treatment and analyzed to ascertain what is sufficient to yield properly converged data. To determine a minimal yet physically accurate active occupied orbital space we have systematically increased our correlation space from valence $5s5p$ to sub-valence $4s4p4d$. We used for the xenon dimer an energy cutoff in the virtual space of $40 E_h$, but a Mulliken population analysis was carried out in order to ensure that all correlating functions were retained.

Table 1 comprises our results for the equilibrium bond length (r_e), harmonic frequency (ω_e) and dissociation energy (D_e) of the xenon dimer. Compared to the QZ basis set calculations with the TZ basis set yield a significant elongation of r_e ($> 0.1 \text{ \AA}$), lowering of harmonic frequencies of $\sim 2\text{--}3 \text{ cm}^{-1}$ and D_e 's reduced by 20%. We are unable to determine to what extent our results are converged at the QZ level, since no Dyal basis sets with higher cardinal number are available. However, upon basis set extrapolation we find, as summarized in Table 1, that the extrapolated results are significantly different from the results obtained with the QZ basis set. We have therefore systematically performed the same extrapolation technique for the radon and eka-radon dimers in our subsequent pure WFT correlation calculations.

Table 1 further shows that even in the extrapolated basis set limit there is a significant spread in the spectroscopic constants obtained by MP2, CCSD and CCSD(T). In fact, we find that MP2 and CCSD in the best basis indeed over- and underbinds the xenon dimer, respectively, in agreement with previous findings (cf. Section 2.2). Therefore, we conclude that we cannot compromise with any lower-level method, but have to use the CCSD(T) method. As shown by Table 1, the deviations of the spectroscopic constants (r_e , ω_e , D_e) with respect to their values derived from experiment are then ($0.017 \text{ \AA}$, 0.8 cm^{-1} , 12 cm^{-1}), respectively, which is quite satisfying.

The effect of correlating sub-valence and outer-core shells can be determined from the CCSD(T)/QZ results outlined in Table 1. Adding the $4d$ shell to the occupied correlation space of the $5s5p$ valence shells changes (r_e , ω_e , D_e) by ($-0.04 \text{ \AA}$, 0.81 cm^{-1} , 13.13 cm^{-1}), whereas the addition of the $4s4p$ shells has hardly any effect. This indicates that saturation with respect to correlated orbitals can to a great extent be reached by including the $(n-1)d$ -shell in addition to the $nsnp$ valence shell of a given noble gas. In subsequent calculations we have therefore correlated $(n-1)dnsnp$.

A final issue to be addressed is whether BSSE-corrected results are to be used or not. BSSE typically leads to overbinding in that the atoms in the dimer calculation benefits from the presence of the basis set of the other atom. Counterpoise-corrected interaction energies for homoatomic dimers A_2 are

given by

$$\Delta E_{int} = E_{A_2}^{A_2} - 2E_A^A + \Delta BSSE; \quad \Delta BSSE = 2(E_A^A - E_A^{AGh}), \quad (11)$$

where atomic energies E_A^{AGh} have been calculated in the full molecular basis by introducing a ghost (Gh) center at the position of the second atom. The usefulness of the counterpoise correction has been challenged in two recent papers by Baerends and co-workers.^{70,71} They have carried out benchmark calculations of the helium and beryllium dimer and find that uncorrected interaction energies overall compare better with (ideally) basis set free reference numbers. They point out that basis set incompleteness is more severe for the dimer than the atom, an imbalance which is aggravated by the improvement of the monomer basis in counterpoise-corrected calculations. Clearly, in a complete basis $E_A^A = E_A^{AGh}$, but this limit is not assured by basis set extrapolation, an issue not discussed by Baerends and co-workers. Indeed, by analysis of their data we find that in general $\Delta BSSE$ is significantly different from zero in the extrapolated basis set limit. From the expected faster convergence of E_A^{AGh} with respect to E_A^A one may expect that the correlation contribution to $\Delta BSSE$ is positive in the extrapolated limit, but curiously this is not always what we observe. Looking at our own data we find that the CP-uncorrected CCSD(T) results agree best with experiment in any finite basis, but not in the extrapolated basis set limit. We have therefore chosen to base our computational protocol on counterpoise-corrected CCSD(T) interaction energies extrapolated to the basis set limit.

Let us now turn to the range-separated approach. Table 1 summarizes the performance of IrWFT-srLDA methods for the xenon dimer. The calculated spectroscopic constants are less sensitive with respect to the choice of basis set as compared to the pure WFT calculations, but the effect is not negligible: the difference between the TZ and QZ basis sets is for either correlation approach on the order of (0.03 Å, 1.2 cm⁻¹, 20 cm⁻¹) for (r_e , ω_e , D_e), respectively. This means in turn that a QZ basis set is required to achieve sufficient accuracy. We next observe, in agreement with previous findings,¹⁶ that the valence-only results for the range-separated methods are in closer agreement to the experimental references than those of their pure WFT counterparts. However, with the inclusion of the 4d shell in the occupied correlation space numbers change significantly: (≥ 0.04 Å, ≥ 1.2 cm⁻¹, ≥ 25 cm⁻¹) for (r_e , ω_e , D_e), respectively. We therefore conclude that similar to the pure WFT case the addition of the ($n-1$)d shell to the active correlation is required for the WFT-srDFT methods. Also with correlation of subvalence we observe a better convergence of the results with regard to the pure WFT correlation model, in particular for CCSD. Still, IrCCSD(T)-srLDA notably outperforms all other methods while showing a consistent behavior with increasing basis set size and correlation

space. The IrCCSD(T)-srLDA approach combined with a QZ basis set thus yields spectroscopic constants within (0.009 Å, 0.5 cm⁻¹, 15 cm⁻¹) for (r_e , ω_e , D_e) of the pure wave function CCSD(T)/CBS reference data. We therefore conclude that IrCCSD(T)-srLDA is indeed a very promising approach for the description of dispersion-bound molecules. We do observe a faster convergence of results with respect to computational parameters, in particular less sensitivity to the inclusion of triple excitations, but not enough to warrant the use of a less expensive computational protocol.

4.2 Rn₂ and Uuo₂

Based on the calibration study discussed in detail in the previous section our computational protocol for the subsequent study of the Rn₂ and Uuo₂ dimers comprises the correlation of the occupied ($n-1$)*dnsnp* shells using the best basis set available, an augmented correlation-consistent QZ basis set. The energy cutoffs in the virtual space were set to 46 and 40 E_h , respectively, for the radon and eka-radon dimers. In case of the pure WFT methods we also carry out extrapolation to the basis set limit according to eqn (10).

Table 2 shows our results for the Rn-dimer at the CCSD(T) level, both for the QZ basis set and extrapolated to the basis set limit. The corresponding IrWFT-srDFT/QZ data shows very close agreement with the pure WFT CCSD(T)/CBS data. The same conclusion holds for the spectroscopic constants of the eka-Radon dimer which are shown in Table 3. Two remarkable features should be noted: i) When including spin-other-orbit interaction through the $X2C_{mmf}^{DCG}$ Hamiltonian, the dissociation energy of eka-Rn₂ is reduced by about 40 %, whereas the effect of this interaction is almost negligible for the lighter homologues. We would like to stress that whereas previous studies have demonstrated considerable weakening of covalent bonds by spin-orbit interaction,⁷²⁻⁷⁷ the present study concerns bonds arising from London dispersion forces and where a substantial weakening is observed upon introduction of a component of the two-electron interaction often ignored in relativistic molecular calculations, namely the spin-other orbit interaction. This is new and merits further study. ii) In spite of the very significant weakening of the eka-Rn₂ bond by inclusion of the Gaunt term, the bond is still markedly stronger than for the lighter homologues, as seen in Figure 1, albeit absent at the HF level.

In Tables 2 and 3 we have listed some results of previous studies. We note that the IrMP2-srDFT spectroscopic constants of Kullie and Saue³² are in line with the present benchmark values, while this is not the case for the values reported by Runeberg and Pyykkö²⁹ and by Nash.³⁰ Runeberg and Pyykkö²⁹ employed large-core pseudo-potentials,^{78,79} calibrated against atomic HF calculations based on the Wood-Boring Hamiltonian⁸⁰ with an effective spin-orbit operator.

Only valence $nsnp$ electrons were treated explicitly and described by a specially designed basis. By comparison with the all-electron basis sets of Dyall we find that the “Basis 2” of Runeberg and Pyykkö are of augmented correlation-consistent TZ quality. Their results are therefore not converged with respect to the basis set and correlated orbitals. Nash³⁰ employs small-core pseudopotentials^{81,82} calibrated against atomic HF calculations based on the Dirac-Coulomb Hamiltonian. Although Nash correlates $(n-1)s(n-1)p(n-1)dnsp$ electrons, his 6sd6p2pf1g valence basis is clearly too small. Runeberg and Pyykkö²⁹ as well as Nash³⁰ include spin-orbit interaction in their calculations, but not spin-other-orbit interaction, which we have seen is critical for the proper description of bonding in eka-Rn₂.

5 Summary and Outlook

We have reported spectroscopic parameters for the homoatomic dimers of xenon, radon and eka-radon obtained with the eXact 2-Component (X2C) molecular-mean field Hamiltonian at the CCSD(T) level and extrapolated to the complete basis set limit, at which counterpoise corrected results seem to be more reliable than uncorrected ones. We also report the very first IrCC-srDFT implementation at the 2- and 4-component relativistic level. The IrCCSD(T)-srLDA/QZ results are in general in rather close agreement with the CCSD(T)/CBS results. Although we observe a somewhat faster convergence of the range-separated results with respect to the number of correlating orbitals, choice of basis set and, in particular, inclusion of triples, in practice this does not allow us to proceed with a computationally less expensive protocol.

Our results confirm the previous IrMP2-srDFT numbers reported by Kullie and Saue,³² notably an almost fourfold increase at the DC level of the binding energy in going from the radon to the eka-radon dimer. However, we also find that the dissociation energy of the eka-Rn₂ dimer is reduced by about 40 % upon the inclusion of spin-other orbit interaction. Yet the bonding in eka-Rn₂ dimer is markedly stronger than in the lighter homologues. This may suggest contributions of covalent bonding to the bonding picture, which clearly deserves further attention, although we find that Uuo₂ is unbound at the HF level. It will therefore be interesting to study the bulk behavior of this superheavy element.

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References

- 1 P. Hobza and R. Zahradnik, *Chem. Rev.*, 1988, **88**, 871–897.
- 2 M. Pitoňák, P. Neogrády, J. Černý, S. Grimme and P. Hobza, *ChemPhysChem*, 2009, **10**, 282–289.
- 3 S. Grimme, *J. Chem. Phys.*, 2003, **118**, 9095–9102.
- 4 K. Burke, *J. Chem. Phys.*, 2012, **136**, 150901.
- 5 S. Kristyán and P. Pulay, *Chem. Phys. Lett.*, 1994, **229**, 175 – 180.
- 6 P. Hobza, J. Šponer and T. Reschel, *J. Comput. Chem.*, 1995, **16**, 1315–1325.
- 7 E. R. Johnson and A. D. Becke, *J. Chem. Phys.*, 2005, **123**, 024101.
- 8 A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.*, 2009, **102**, 073005.
- 9 T. Sato and H. Nakai, *J. Chem. Phys.*, 2009, **131**, 224104.
- 10 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.
- 11 S. Grimme, *WIREs: Comput. Mol. Sci.*, 2011, **1**, 211–228.
- 12 J. Klimeš and A. Michaelides, *J. Chem. Phys.*, 2012, **137**, 120901.
- 13 C. Corminboeuf, *Acc. Chem. Res.*, 2014, **47**, 3217–3224.
- 14 N. Mardirossian and M. Head-Gordon, *J. Chem. Phys.*, 2014, **140**, 18A527.
- 15 A. Savin, in *Recent developments of modern density functional theory*, ed. J. M. Seminario, Elsevier, Amsterdam, 1996, pp. 327–357.
- 16 E. Goll, H.-J. Werner and H. Stoll, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3917–3923.
- 17 T. Van Mourik, A. K. Wilson and T. H. Dunning, *Mol. Phys.*, 1999, **96**, 529–547.
- 18 T. van Mourik and R. J. Gdanitz, *J. Chem. Phys.*, 2002, **116**, 9620–9623.
- 19 P. Slavek, R. Kalus, P. Paška, I. Odvárková, P. Hobza and A. Malijevský, *J. Chem. Phys.*, 2003, **119**, 2102–2119.
- 20 R. Hellmann, E. Bich and E. Vogel, *Mol. Phys.*, 2008, **106**, 133–140.
- 21 B. Jäger, R. Hellmann, E. Bich and E. Vogel, *Mol. Phys.*, 2009, **107**, 2181–2188.
- 22 A. Tkatchenko, R. A. DiStasio, M. Head-Gordon and M. Scheffler, *J. Chem. Phys.*, 2009, **131**, 094106.
- 23 M. Przybytek, W. Cencek, J. Komasa, G. Łach, B. Jeziorski and K. Szalewicz, *Phys. Rev. Lett.*, 2010, **104**, 183003.
- 24 K. Patkowski and K. Szalewicz, *J. Chem. Phys.*, 2010, **133**, 094304.
- 25 K. Patkowski, *J. Chem. Phys.*, 2012, **137**, 034103.
- 26 D. Roy, M. Marianski, N. T. Maitra and J. J. Dannenberg, *J. Chem. Phys.*, 2012, **137**, 134109.
- 27 W. Cencek, M. Przybytek, J. Komasa, J. B. Mehl, B. Jeziorski and K. Szalewicz, *J. Chem. Phys.*, 2012, **136**, 224303.
- 28 F. Tran and J. Hutter, *J. Chem. Phys.*, 2013, **138**, 204103.
- 29 N. Runeberg and P. Pyykkö, *Int. J. Quantum Chem*, 1998, **66**, 131–140.
- 30 C. S. Nash, *J. Phys. Chem. A*, 2005, **109**, 3493–3500.
- 31 V. Pershina, A. Borschevsky, J. Anton and T. Jacob, *J. Chem. Phys.*, 2010, **132**, 194314.
- 32 O. Kullie and T. Saue, *Chem. Phys.*, 2012, **395**, 54 – 62.
- 33 V. V. Avrorin, R. N. Krasikova, V. D. Nefedov and M. A. Toropova, *Russ. Chem. Rev.*, 1982, **51**, 12.
- 34 L. Stein, *Radiochim. Acta*, 1983, **32**, 163–172.
- 35 B. F. Thornton and S. C. Burdette, *Nat. Chem.*, 2013, **5**, 804.
- 36 Y. Oganessian, V. Utyonkov, Y. Lobanov, F. Abdullin, A. Polyakov, R. Sagaidak, I. Shirokovsky, Y. Tsyganov, A. Voinov, G. Gulbekian, S. Bogomolov, B. Gikal, A. Mezentsev, S. Iliev, V. Subbotin, A. Sukhov, K. Subotic, V. Zagrebaev, G. Vostokin, M. Itkis, K. Moody, J. Patin, D. Shaughnessy, M. Stoyer, N. Stoyer, P. Wilk, J. Kenneally, J. Landrum, J. Wild and R. Loughheed, *Phys. Rev. C*, 2006, **74**, 044602.

- 37 F. P. Heßberger, *ChemPhysChem*, 2013, **14**, 483–489.
- 38 A. Türlér and V. Pershina, *Chem. Rev.*, 2013, **113**, 1237–1312.
- 39 M. Schädel, *Radiochim. Acta*, 2012, **100**, 579–604.
- 40 *The Chemistry of Superheavy Elements*, ed. M. Schädel and D. Shaughnessy, Springer, Heidelberg, 2014.
- 41 T. Saue, *ChemPhysChem*, 2011, **12**, 3077–3094.
- 42 J. Sikkema, L. Visscher, T. Saue and M. Iliaš, *J. Chem. Phys.*, 2009, **131**, 124116.
- 43 E. J. Baerends, W. H. E. Schwarz, P. Schwerdtfeger and J. G. Snijders, *J. Phys. B: Atomic, Molecular and Optical Physics*, 1990, **23**, 3225.
- 44 V. Kellö and A. J. Sadlej, *Int. J. Quantum Chem.*, 1998, **68**, 159–174.
- 45 K. G. Dyall, *Int. J. Quantum Chem.*, 2000, **78**, 412–421.
- 46 S. M. Cybulski and M. L. Lytle, *J. Chem. Phys.*, 2007, **127**, 141102.
- 47 A. Hesselmann, *J. Chem. Phys.*, 2008, **128**, 144112.
- 48 A. Szabo and N. S. Ostlund, *J. Chem. Phys.*, 1977, **67**, 4351–4360.
- 49 B. W. Hopkins and G. S. Tschumper, *J. Phys. Chem. A*, 2004, **108**, 2941–2948.
- 50 A. V. Copan, A. Y. Sokolov and H. F. Schaefer, *J. Chem. Theory Comput.*, 2014, **10**, 2389–2398.
- 51 K. E. Riley, M. Pitoňák, P. Jurečka and P. Hobza, *Chem. Rev.*, 2010, **110**, 5023–5063.
- 52 J. Řezáč, K. E. Riley and P. Hobza, *J. Chem. Theory Comput.*, 2011, **7**, 2427–2438.
- 53 J. Řezáč, K. E. Riley and P. Hobza, *J. Chem. Theory Comput.*, 2011, **7**, 3466–3470.
- 54 W. Yang, *J. Chem. Phys.*, 1998, **109**, 10107–10110.
- 55 J. K. Pedersen, *Dissertation*, Department of Chemistry, University of Southern Denmark, 2004.
- 56 I. C. Gerber and J. G. Ángyán, *Chem. Phys. Lett.*, 2005, **415**, 100 – 105.
- 57 E. Fromager and H. J. A. Jensen, *Phys. Rev. A*, 2008, **78**, 022504.
- 58 J. G. Ángyán, *Phys. Rev. A*, 2008, **78**, 022510.
- 59 T. Helgaker, W. Klopper, H. Koch and J. Noga, *J. Chem. Phys.*, 1997, **106**, 9639.
- 60 A. Halkier, T. Helgaker, P. Jørgensen, W. Klopper, H. Koch, J. Olsen and A. K. Wilson, *Chem. Phys. Lett.*, 1998, **286**, 243 – 252.
- 61 O. Franck, B. Mussard, E. Luppi and J. Toulouse, *J. Chem. Phys.*, 2015, **142**, 074107.
- 62 DIRAC, a relativistic ab initio electronic structure program, Release DIRAC13 (2013), written by L. Visscher, H. J. Aa. Jensen, R. Bast, and T. Saue, with contributions from V. Bakken, K. G. Dyall, S. Dubillard, U. Ekström, E. Eliav, T. Enevoldsen, E. Faßhauer, T. Fleig, O. Fossgaard, A. S. P. Gomes, T. Helgaker, J. K. Lærdahl, Y. S. Lee, J. Henriksson, M. Iliaš, Ch. R. Jacob, S. Knecht, S. Komorovský, O. Kulie, C. V. Larsen, H. S. Nataraj, P. Norman, G. Olejniczak, J. Olsen, Y. C. Park, J. K. Pedersen, M. Pernpointner, K. Ruud, P. Salek, B. Schimelpfennig, J. Sikkema, A. J. Thorvaldsen, J. Thyssen, J. van Stralen, S. Villaume, O. Visser, T. Winther, and S. Yamamoto (see <http://www.diracprogram.org>).
- 63 L. Visscher and K. G. Dyall, *At. Data Nucl. Data Tables*, 1997, **67**, 2007.
- 64 K. Dyall, *Theor. Chem. Acc.*, 2006, **115**, 441–447.
- 65 K. Dyall, *Theor. Chem. Acc.*, 2012, **131**, 1172.
- 66 P. M. W. Gill, R. D. Adamson and J. Pople, *Mol. Phys.*, 1996, **88**, 1005.
- 67 J. Toulouse, A. Savin and H.-J. Flad, *Int. J. Quant. Chem.*, 2004, **100**, 1047–1056.
- 68 E. Fromager, J. Toulouse and H. J. A. Jensen, *J. Chem. Phys.*, 2007, **126**, 074111.
- 69 S. Boys and F. Bernardi, *Mol. Phys.*, 1970, **19**, 553–566.
- 70 X. W. Sheng, L. Mentel, O. V. Gritsenko and E. J. Baerends, *J. Comp. Chem.*, 2011, **32**, 2896–2901.
- 71 L. M. Mentel and E. J. Baerends, *J. Chem. Theory Comput.*, 2014, **10**, 252–267.
- 72 P. A. Christiansen and K. S. Pitzer, 1981, **74**, 1162.
- 73 P. Hafner, P. Habitz, Y. Ishikawa, E. Wechsel-Trakowski and W. H. E. Schwarz, 1981, **80**, 311.
- 74 T. Saue, K. Fægri and O. Gropen, *Chem. Phys. Lett.*, 1996, **263**, 360.
- 75 Y.-K. Han, C. Bae and Y. S. Lee, 1999, **110**, 8969.
- 76 Y.-K. Han, C. Bae, S.-K. Son and Y. S. Lee, 2000, **112**, 2684.
- 77 K. Fægri and T. Saue, 2001, **115**, 2456.
- 78 A. Nicklass, M. Dolg, H. Stoll and H. Preuss, *J. Chem. Phys.*, 1995, **102**, 8942.
- 79 W. Küchle, M. Dolg, H. Stoll and H. Preuss, *Mol. Phys.*, 1991, **74**, 1245–1263.
- 80 J. H. Wood and A. M. Boring, *Phys. Rev. B*, 1978, **18**, 2701–2711.
- 81 C. S. Nash and B. E. Bursten, *J. Phys. Chem. A*, 1999, **103**, 402–410.
- 82 C. S. Nash, B. E. Bursten and W. C. Ermler, *J. Chem. Phys.*, 1997, **106**, 5133–5142.
- 83 J. Ogilvie and F. Y. Wang, *J. Mol. Struct.*, 1992, **273**, 277 – 290.
- 84 K. A. Peterson, D. Figgen, E. Goll, H. Stoll and M. Dolg, *J. Chem. Phys.*, 2003, **119**, 11113–11123.

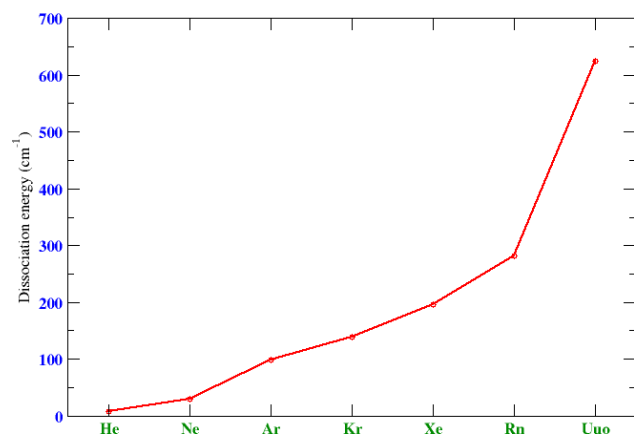


Fig. 1 Dissociation energies D_e (in cm⁻¹) for the homonuclear rare gas dimers. The first five data points are derived from experiment,⁸³ whereas the final two points correspond to the values obtained in the present work with the $X2C_{mmf}^{DCG}$ Hamiltonian at CCSD(T) level and extrapolated to the basis set limit.

Table 1 Spectroscopic constants for the xenon dimer. dyall.acv ∞ z refers to extrapolated basis using eqn (10) with X=4. CP refers to counterpoise correction. ECP stands for Effective Core Potential. Bold numbers are best numbers for each choice of Hamiltonian and method.

Method	Correlating Orbitals	Hamiltonian	Basis	$r_e/\text{\AA}$	ω_e/cm^{-1}	D_e/cm^{-1}	CP
MP2	5s5p	$X2C_{mmf}^{DC}$	dyall.acv3z	4.491	18.01	165.16	x
			dyall.acv4z	4.392	20.76	204.48	x
CCSD			dyall.acv3z	4.673	13.98	98.43	x
			dyall.acv4z	4.564	15.99	120.98	x
CCSD(T)			dyall.acv3z	4.585	15.81	127.20	x
			dyall.acv4z	4.465	18.67	162.62	x
MP2-srLDA			dyall.acv3z	4.431	18.54	173.54	x
			dyall.acv4z	4.404	19.56	189.98	x
CCSD-srLDA			dyall.acv3z	4.440	18.37	171.40	x
			dyall.acv4z	4.408	19.55	190.69	x
CCSD(T)-srLDA			dyall.acv3z	4.429	18.75	179.28	x
			dyall.acv4z	4.396	19.99	200.49	x
MP2	4d5s5p	$X2C_{mmf}^{DC}$	dyall.acv3z	4.375	20.64	213.90	x
			dyall.acv4z	4.349	21.40	230.88	x
			dyall.acv ∞ z	4.275	23.87	267.32	x
			dyall.acv ∞ z	4.250	24.68	283.57	x
CCSD			dyall.acv3z	4.213	26.21	311.14	x
			dyall.acv3z	4.187	27.16	327.80	x
			dyall.acv4z	4.644	14.19	102.15	x
			dyall.acv4z	4.610	14.96	112.81	x
CCSD(T)			dyall.acv3z	4.536	16.30	124.95	x
			dyall.acv3z	4.510	16.85	132.95	x
			dyall.acv ∞ z	4.466	17.99	144.53	x
			dyall.acv ∞ z	4.444	18.41	151.01	x
MP2-srLDA			dyall.acv3z	4.540	16.52	137.53	x
			dyall.acv3z	4.508	17.40	151.13	x
CCSD-srLDA			dyall.acv4z	4.421	19.48	175.75	x
			dyall.acv4z	4.396	20.11	186.64	x
CCSD(T)-srLDA			dyall.acv ∞ z	4.346	21.73	208.69	x
			dyall.acv ∞ z	4.324	22.28	217.67	x
			dyall.acv3z	4.364	20.58	213.29	x
			dyall.acv4z	4.337	21.70	233.59	x
CCSD-srLDA			dyall.acv3z	4.399	19.54	193.04	x
			dyall.acv4z	4.367	20.78	215.03	x
CCSD(T)-srLDA			dyall.acv3z	4.388	19.93	201.65	x
			dyall.acv4z	4.355	21.25	225.76	x
MP2	4s4p4d5s5p	$X2C_{mmf}^{DC}$	dyall.acv3z	4.373	20.71	214.94	x
			dyall.acv4z	4.272	23.94	268.91	x
CCSD			dyall.acv3z	4.646	14.17	101.96	x
			dyall.acv4z	4.537	16.26	124.51	x
CCSD(T)			dyall.acv3z	4.540	16.55	138.01	x
			dyall.acv4z	4.420	19.49	176.17	x
MP2-srLDA			dyall.acv3z	4.362	20.64	214.42	x
			dyall.acv3z	4.398	19.58	193.73	x
CCSD-srLDA			dyall.acv3z	4.386	19.97	202.36	x
			dyall.acv3z	4.386	19.97	202.36	x
CCSD(T)	4d5s5p	$X2C_{mmf}^{DCG}$	dyall.acv4z	4.422	19.49	176.14	x
			dyall.acv ∞ z	4.347	21.74	209.17	x
MP2-srLDA ³²	4d5s5p	DC	dyall.acv4z	4.337	21.7	233.6	x
CCSD(T) ²⁹	5s5p	ECP46MWB ⁷⁸	"Basis 2"	4.525	17.6	156.5	x
CCSD(T)-srPBE ¹⁶	5s5p	ECP28MDF ⁸⁴	aug-cc-pVQZ	4.334	20.5	197.5	x
Exp. ⁸³				4.363	20.90	196.20	

Table 2 Spectroscopic constants for the radon dimer. dyall.acv ∞ z refers to extrapolated basis using eqn (10) with X=4. CP refers to counterpoise correction. ECP stands for Effective Core Potential. Bold numbers are best numbers for each choice of Hamiltonian and method.

Method	Correlating Orbitals	Hamiltonian	Basis	$r_e/\text{\AA}$	ω_e/cm^{-1}	D_e/cm^{-1}	CP
MP2	5d6s6p	$X2C_{mmf}^{DC}$	dyall.acv4z	4.343	20.47	364.40	x
				4.323	21.04	385.70	
			dyall.acv ∞ z	4.280	22.43	427.31	x
CCSD			dyall.acv4z	4.263	23.01	449.82	
				4.617	13.93	168.56	x
			dyall.acv ∞ z	4.596	14.42	179.55	
CCSD(T)			dyall.acv4z	4.617	15.45	197.25	x
				4.528	15.91	207.22	
			dyall.acv ∞ z	4.502	16.56	235.56	x
MP2-srLDA			dyall.acv4z	4.483	17.06	249.70	
				4.424	18.54	282.80	x
			dyall.acv ∞ z	4.412	18.97	294.95	
CCSD-srLDA			dyall.acv4z	4.388	19.06	323.68	x
CCSD(T)-srLDA			dyall.acv4z	4.432	17.87	284.73	x
			dyall.acv4z	4.418	18.31	301.02	x
MP2	5d6s6p	$X2C_{mmf}^{DCG}$	dyall.acv4z	4.346	20.49	363.58	x
				4.282	22.46	426.99	x
			dyall.acv ∞ z	4.282	22.46	426.99	x
CCSD			dyall.acv4z	4.621	13.91	166.65	x
				4.547	15.44	195.57	x
			dyall.acv ∞ z	4.547	15.44	195.57	x
CCSD(T)			dyall.acv4z	4.506	16.55	233.82	x
				4.427	18.53	281.41	x
			dyall.acv ∞ z	4.427	18.53	281.41	x
PBE ³¹	all	DC		4.646	15	193.6	
MP2-srLDA ³²	5d6s6p	DC	dyall.acv4z	4.387	19.0	323.9	x
CCSD(T) ²⁹	6s6p	ECP78MWB ⁷⁹	“Basis 2”	4.639	14.9	222.6	x
CCSD(T) ³⁰	5s5p5d6s6p	RECP60(DC) ⁸¹	6sd6p2pf1g	4.73		129.1	

Table 3 Spectroscopic constants for the eka-Radon dimer dyall.acv ∞ z refers to extrapolated basis using eqn (10) with X=4. CP refers to counterpoise correction. ECP stands for Effective Core Potential. Bold numbers are best numbers for each choice of Hamiltonian and method.

Method	Correlating Orbitals	Hamiltonian	Basis	$r_e/\text{\AA}$	ω_e/cm^{-1}	D_e/cm^{-1}	CP
MP2	6d7s7p	$X2C_{mmf}^{DC}$	dyall.acv4z	4.184	26.52	1258.87	x
				4.169	27.60	1286.93	
			dyall.acv ∞ z	4.136	28.11	1389.73	x
CCSD				4.130	28.43	1400.40	
			dyall.acv4z	4.435	18.85	765.65	x
				4.424	19.55	777.00	
CCSD(T)			dyall.acv ∞ z	4.383	20.13	832.78	x
				4.380	19.87	832.28	
			dyall.acv4z	4.338	21.70	927.73	x
MP2-srLDA				4.327	22.51	942.52	
			dyall.acv ∞ z	4.280	23.39	1033.53	x
				4.280	23.45	1032.71	
CCSD-srLDA			dyall.acv4z	4.205	25.51	1198.53	x
CCSD(T)-srLDA			dyall.acv4z	4.254	23.77	1075.93	x
			dyall.acv4z	4.240	24.32	1121.05	x
MP2	6d7s7p	$X2C_{mmf}^{DCG}$	dyall.acv4z	4.223	25.00	840.59	x
				4.172	26.67	966.61	x
			dyall.acv ∞ z	4.172	26.67	966.61	x
CCSD			dyall.acv4z	4.503	17.02	372.01	x
				4.445	18.27	434.14	x
			dyall.acv ∞ z	4.445	18.27	434.14	x
CCSD(T)			dyall.acv4z	4.393	19.94	524.18	x
				4.329	21.74	624.24	x
			dyall.acv ∞ z	4.329	21.74	624.24	x
PBE ³¹	all	DC		4.375	20	427.5	
MP2-srLDA ³²	6d7s7p	DC	dyall.acv4z	4.205	26.3	1199.1	x
CCSD(T) ³⁰	6s6p6d7s7p	RECP92(DC) ⁸²	6sd6p2pf1g	4.57		500.1	