

Supplementary Information for:

**Relativistic Quantum Chemical Calculations Show that the Uranium Molecule U₂
Has a Quadruple Bond**

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I. METHODS

A. Computational details

The atomic data reported in Fig. 1 of the main text as well as Supplementary Table 1 were obtained from 4-component atomic average-of-configuration Hartree-Fock calculations¹ with the uncontracted [33s29p20d15f6g2h] `dya11.cv3z` basis set². The fully relativistic results were obtained using the Dirac–Coulomb–Gaunt Hamiltonian, whereas the scalar-relativistic results were obtained using its spin-free variant³. The non-relativistic results are based on the 4-component *non*-relativistic Lévy–Leblond Hamiltonian^{3,4}.

All molecular calculations were carried out with the CASSCF/RASSCF implementation in the DIRAC program package¹ within the exact 2-component (X2C) Hamiltonian framework⁵. The X2C Hamiltonian combines computational efficiency with the accuracy of its parent four-component Dirac Hamiltonian^{6,7} while encompassing all important scalar-relativistic and spin-orbit coupling effects, also for actinide complexes⁷. Two-electron picture-change corrections to the spin-same and spin-other orbit interaction stemming from the two-electron Coulomb and Gaunt interactions, respectively⁸, are considered in an atomic mean-field fashion⁹.

It should be noted that spin-orbit coupling breaks spin symmetry. However, in the absence of external magnetic fields, orbitals are still doubly degenerate,¹⁰ but now due to time reversal symmetry,¹¹ and spinorbital partners are replaced by *Kramers pairs*.¹²

An alternative to our fully variational treatment of SO interaction is a two-step SO procedure, where for instance a scalar-relativistic CASSCF calculation is followed by a small configuration interaction problem with a model SO Hamiltonian. This is a perfectly adequate method for many cases (see for example Refs. 13 and 14 as well as references therein), but comes with some limitations: The success of such a procedure relies on several crucial assumptions, namely the additivity of electron correlation and SO effects, weak polarization of orbitals due to SO interaction, or both. Furthermore, in order to possibly reach convergence for the resulting SO-coupled eigenstates one has to take into account an *a priori* unknown, yet, sufficiently large number of spin-free electronic states for the evaluation of the SO Hamiltonian matrix elements. Consequently, the predictive

potential of the above sketched two-step SO model is intrinsically limited for any finite set of spin-free states.

We apply the standard notation $\text{RAS}(n, l, m; i, j, k)^{15}$ to indicate our RASSCF model, where n is the number of active electrons, l the maximum number of holes in RAS1, m the maximum number of electrons in RAS3, and i, j and k the number of orbitals (i.e. Kramers pairs) in the RAS1, RAS2 and RAS3 orbital spaces, respectively. Two different active spaces have been considered in this work. The first active space corresponds to a CAS-type model and comprises six electrons distributed in 20 Kramers pairs (CAS(6,20)). In this model all $5f$ and $6d$ Kramers pairs except for the strong-bonding (anti-bonding) $6d$ Kramers pairs of approximate π_u (π_g) symmetry as well as the $7s_{\sigma_g}$ ($7s_{\sigma_u}$). In accordance with the active orbital space considered by Gagliardi and Roos¹⁶ the latter were kept inactive (empty). In the $\text{RAS}(12,2,8;6,0,20)\text{SCF}$ calculations we then included the strong bonding and anti-bonding orbitals in RAS1 ($i = 6$) thus making both orbital sets active and yielding a distribution of six electrons in six Kramers pairs. In addition, up to double excitations are considered into the RAS3 space (corresponding to $l = 2$ holes in RAS1 and at most an accumulated maximum of $m = 8$ electrons in RAS3). The RAS3 space comprises the above discussed CAS(6,20) space. Note that in this model the RAS2 orbital space remains empty ($j = 0$). A compelling feature of the chosen RAS model in contrast to the CAS model is that it allows us to dissociate the U_2 molecule into two ground-state atoms, and the RAS model is therefore used for evaluation of dissociation energies. A schematic overview of both computational models is given in Supplementary Fig. 1. Note that the full CAS(12,26) active orbital space is computationally not feasible with current state-of-the art relativistic CASSCF implementations. The active space for the CASSCF calculations of the dication U_2^{2+} (see Supplementary Fig. 5) comprised four electrons distributed in 20 Kramers pairs (CAS(4,20)) and corresponds to the CAS(6,20) orbital space model of the neutral parent molecule by removing two electrons.

All calculations were performed with linear supersymmetry, implemented at the correlated level in the course of this work, where the full linear double group was approximated by a finite D_{32h} representation. We employed two different basis sets in uncontracted form for the CASSCF and RASSCF calculations, namely the all-electron dual family basis set by de Jong¹⁷ augmented with additional three g functions¹⁸ yielding a set

of [26s21p17d12f3g] primitives denoted as `deJong+3g`, which has successfully been used in earlier actinide studies^{19,20}, as well as the larger core-valence correlation-consistent [33s29p20d15f6g2h] basis set of triple- ζ quality by Dyal² denoted as `dya11.cv3z` for the three lowest-lying electronic states found with the `deJong+3g` basis set. We did not use the same basis sets as in Refs. 16 and 21 due to a different choice of Hamiltonian. However, the wave function and chemical bond analysis presented in this work are based on well-defined quantities — the natural orbital occupation numbers — which are stable measures with respect to variations in the basis set and the quality of the wave function, provided that the most important active orbitals are included in the wave function optimization.²¹ In order to estimate the effect on including more dynamical correlation, we carried out sample multi-reference configuration interaction (MRCI) calculations for the $\Omega = 8_g$ and $\Omega = 9_g$ states close to their respective U-U equilibrium bond length at $R_{U-U} = 2.53 \text{ \AA}$ based on a RAS(12,4,10;6,0,20)-CI model with the `deJong+3g` basis set. For either electronic state the corresponding, optimized RAS(12,2,8;6,0,20)-SCF orbitals served as reference MO basis. Compared to the RASSCF calculations, the number of allowed holes (electrons) in RAS1 (RAS3) was raised by 2, i.e. $l_{\text{RASCI}} = l_{\text{RASSCF}} + 2$ ($m_{\text{RASCI}} = m_{\text{RASSCF}} + 2$), leading to a variational CI space of more than 1.6 billion Slater determinants, i.e., approximately three times larger than the CI space of the parent RASSCF active orbital space model. By these means, the inclusion of more dynamical correlation led to an increase of the energy gap Δ_Ω between the $\Omega = 9_g$ and $\Omega = 8_g$ states by 8%, namely from 3881 cm^{-1} to 4179 cm^{-1} , thus favoring our conclusions with respect to the $\Omega = 9_g$ being the ground electronic state in U_2 . In summary, the sample MRCI calculations did not reveal any significant differential correlation effects for the lowest electronic states that could have an impact on our conclusions.

The binding energy was estimated from a CASSCF calculation on the $J = 6$ electronic ground state of the uranium atom using the same basis set as for the molecule and with the full set of valence orbitals ($7s, 6d, 5f$) included in the active orbital space. To correct for the basis set superposition error within a counterpoise correction scheme²², the atomic calculation was carried out in the full diatomic basis set. As the correlation treatment of the atom is better than of the molecule due to the difference in the quality of the active orbital spaces, the reported data should be regarded as a lower bound to the true binding

energy.

The nature of the molecular NOs as well as the atomic configuration of uranium in each electronic state shown in Table 1 and Supplementary Table 2, respectively, were extracted by Mulliken population analysis²³. Such an analysis is known to be not reliable due to its strong basis set dependence (see Ref. 24 for an example), but in the present case this is not an issue due to the high symmetry of the molecule.

In linear molecules without strong spin-orbit coupling, corresponding to Hund's case (a), the total angular momentum along the internuclear axis Ω is described as

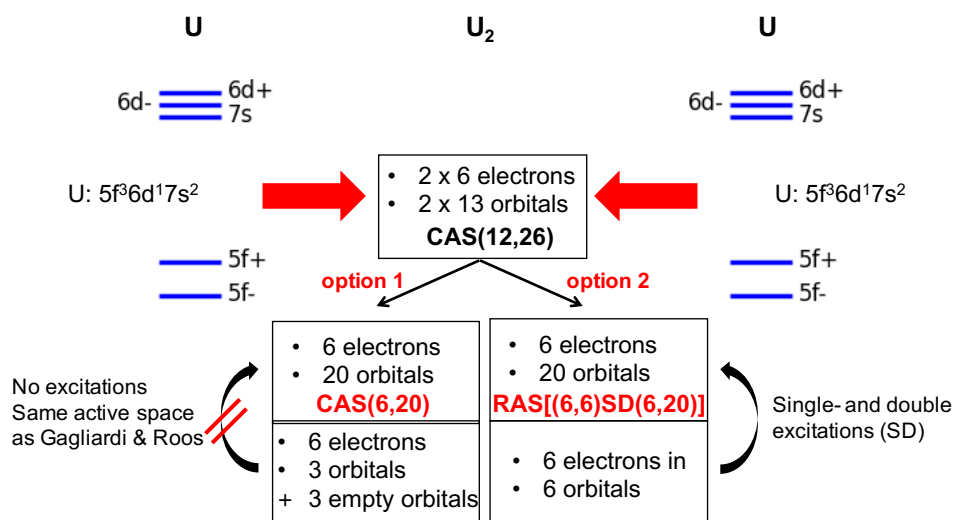
$$\Omega = \Sigma + \Lambda, \tag{1}$$

where $\Lambda \equiv |M_L|$ is the projection of the total orbital angular momentum along the internuclear axis and where $\Sigma \equiv M_S$ is the projection of the total spin along the same direction²⁵. U_2 corresponds clearly to Hund's case (c), where strong spin-orbit coupling implies that Σ and Λ are no longer approximately good quantum numbers, and only the sum Ω is left as a valid quantum number. For comparison with scalar-relativistic results, we analyze the projection of spin and orbital angular momentum quantum numbers on the internuclear axis (arbitrarily chosen here to coincide with the z -axis) of a given Ω state by calculating the expectation values of the operators \hat{S}_z and \hat{L}_z , respectively.

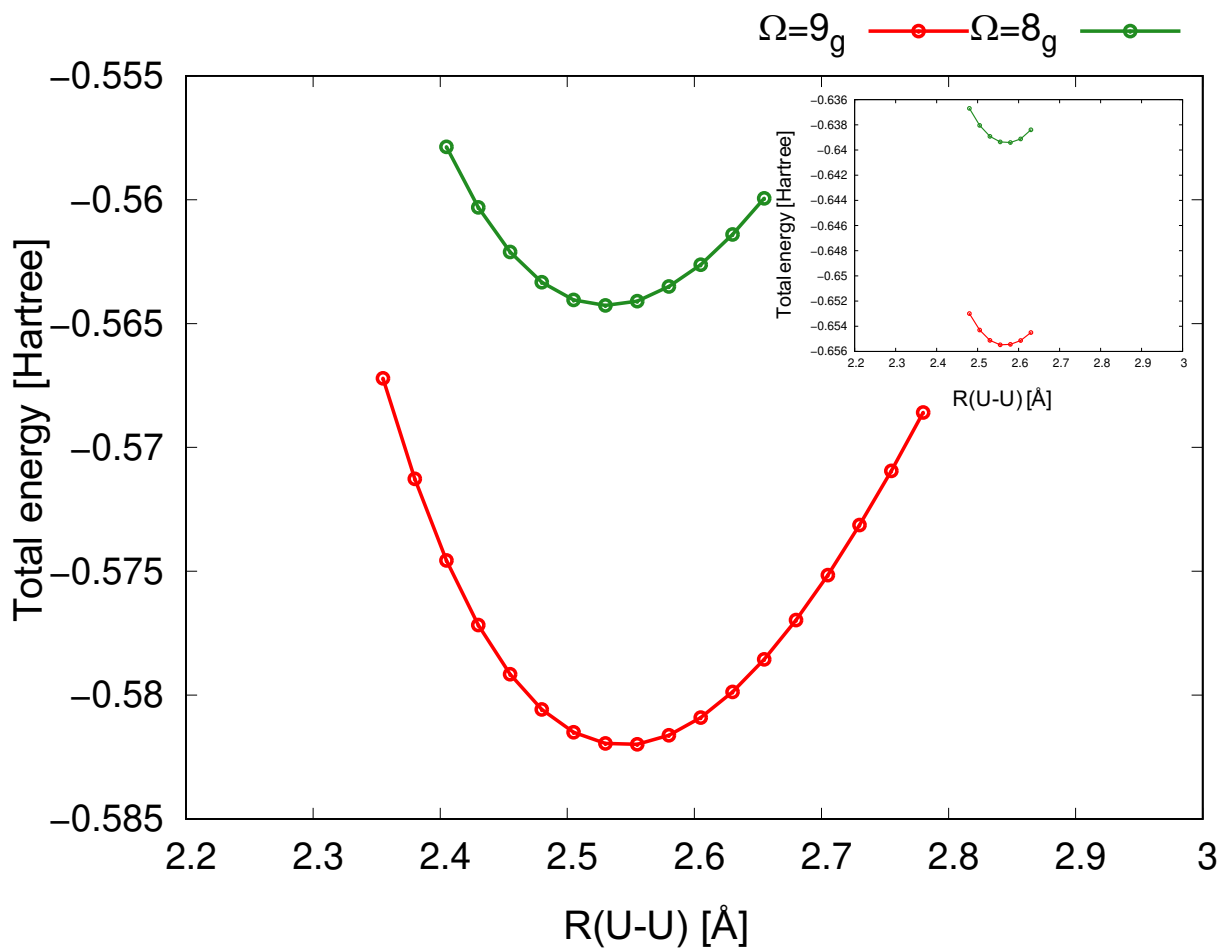
B. Code availability

All calculations in this study were performed with the DIRAC program package. Its source code is available free-of-charge upon request at <http://diracprogram.org>.

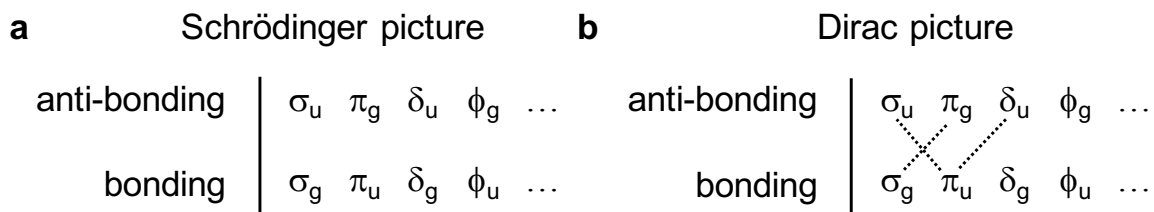
II. FIGURES



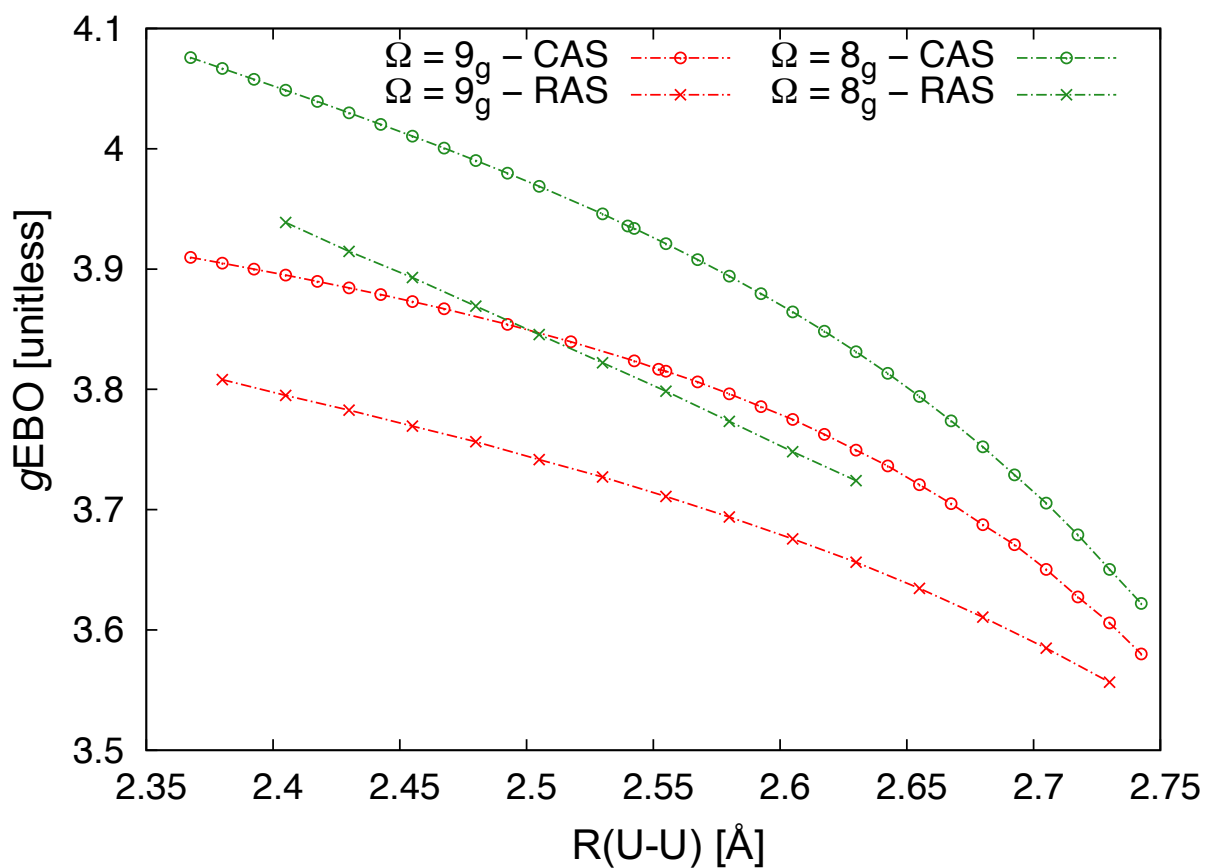
Supplementary Figure 1. Active spaces used in the CAS(6,20)SCF and RAS(12,2,8;6,0,20)SCF calculations. The CAS(6,20) space corresponds to the orbital space proposed by Gagliardi and Roos¹⁶.



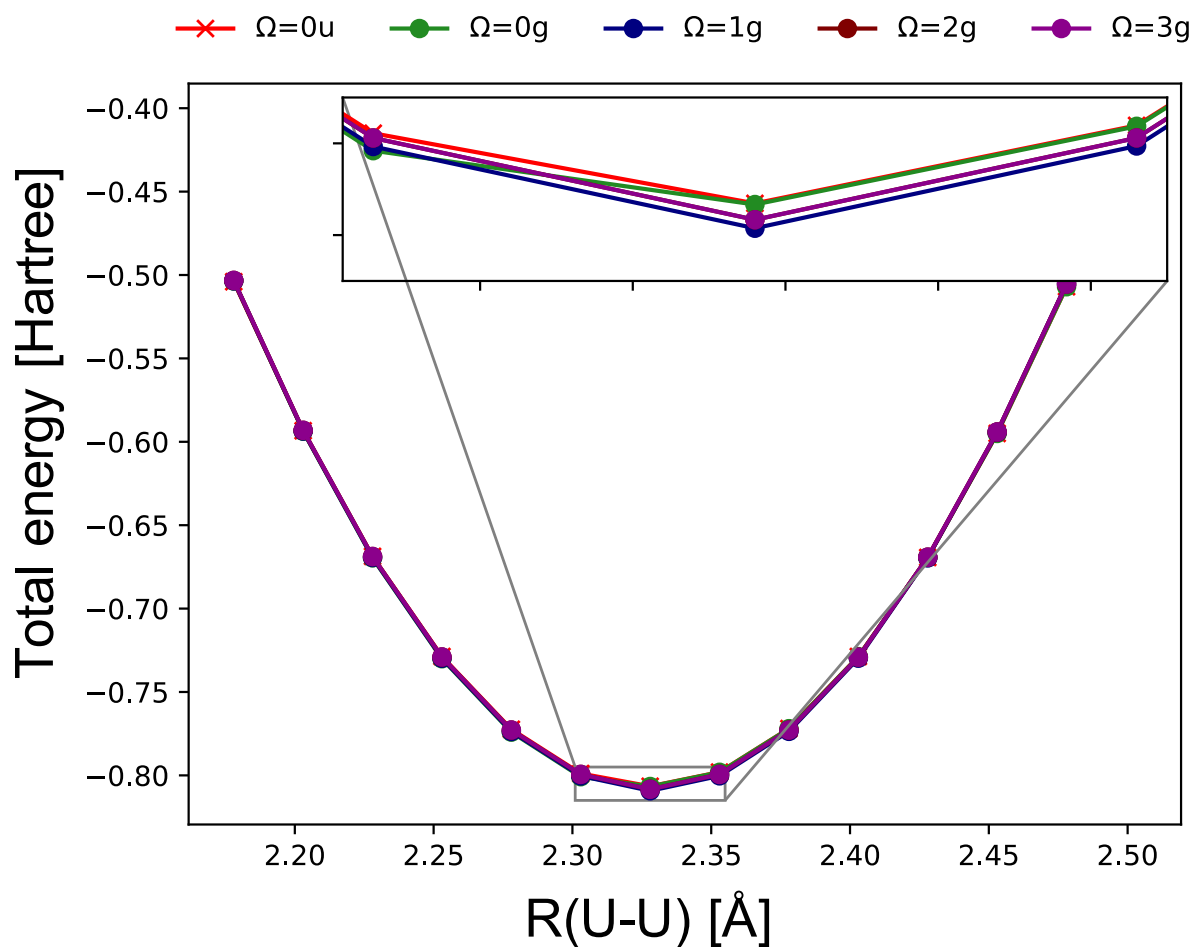
Supplementary Figure 2. RASSCF potential energy curves for the lowest two electronic states of U_2 around the equilibrium structure calculated with the uncontracted $[26s21p17d12f3g]$ de-Jong+3g basis set¹⁷. The inset in the upper right corner shows the RASSCF potential energy curves for the same two electronic states of U_2 around the equilibrium structure calculated with the uncontracted $[33s29p20d15f6g2h]$ dya11.cv3z basis set². Color and symbol codes for the electronic states are in both cases identical. Absolute energies are reported with an offset of -56075 Hartree.



Supplementary Figure 3. Classification of bonding and anti-bonding MOs in homonuclear diatomic molecules in a non- or scalar-relativistic framework (panel **a**) . A unique partitioning of MOs into bonding and anti-bonding is no longer possible if SO interaction is present (panel **b**). MOs of the same parity but different angular momentum are allowed to mix as indicated by the dotted lines. For simplicity, a nonrelativistic notation is kept.



Supplementary Figure 4. Generalized effective bond orders (g EBOs) of the $\Omega = 8_g$ and $\Omega = 9_g$ electronic states of U_2 , respectively, as a function of the U-U internuclear distance. The label “CAS” refers to data obtained from CASSCF calculations while “RAS” denotes the corresponding data obtained from RASSCF calculations.



Supplementary Figure 5. CASSCF potential energy curves for the lowest electronic states of U_2^{2+} calculated with the `dya11.cv3z` basis set. The inset shows a zoom of the CASSCF potential energy curves within the indicated equilibrium internuclear distances. Color and symbol codes for the electronic states are in both cases identical. Absolute energies are reported with an offset of -56074 Hartree.

III. TABLES

Supplementary Table 1. Root-mean-squared (rms) values ($\langle r^2 \rangle^{\frac{1}{2}}$) for the radial functions of the frontier atomic orbitals (AOs) of uranium obtained from average-of-configuration Hartree-Fock calculations employing the `dya11.cv3z` basis set. All data in atomic units.

AO	rms	AO	rms	AO	rms
<i>nonrelativistic</i>		<i>scalar-relativistic</i>		<i>relativistic</i>	
7s	5.364	7s	4.639	7s	4.625
6d	3.105	6d	3.518	6d+	3.582
				6d-	3.436
5f	1.394	5f	1.603	5f+	1.629
				5f-	1.581

Supplementary Table 2. Mulliken atomic orbital populations (per atom) for U_2 in different electronic states at their respective equilibrium structures determined from CASSCF calculations.

	Ω	7s	6d	5f
Our work	9 _g	1.02	2.57	2.37
Our work	8 _g	1.03	2.60	2.33
Ref. 21	8 _g	0.94	2.59	2.44

IV. SAMPLE INPUT FILES

A. CASSCF input file for DIRAC

```
**DIRAC
.TITLE
  CASSCF for the uranium dimer in linear symmetry - Omega = 9g state
.WAVE FUNCTION
**INTEGRALS
*READIN
.UNCONTRACT
**HAMILTONIAN
.X2C
.GAUNT
**WAVE FUNCTION
.KRMCSCF
*KRMCSCF
.CI PROGRAM
LUCIAREL
.INACTIVE
  44 45
.GASSH
  1
  10 10
.GASSPC
  6 6
.MK2REF
  0
.MK2DEL
  6
.SYMMETRY
  18g
```

```
.MAX MACRO
16
.MAX MICRO
22
.THRESH
1.0D-3
.DELETE
251..401
251..401
**END OF
```

B. RASSCF input file for DIRAC

```
**DIRAC
.TITLE
RASSCF for the uranium dimer in linear symmetry - Omega = 9g state
.WAVE FUNCTION
**INTEGRALS
*READIN
.UNCONTRACT
**HAMILTONIAN
.X2C
.GAUNT
**WAVE FUNCTION
.KRMCSCF
*KRMCSCF
.CI PROGRAM
LUCIAREL
.INACTIVE
43 43
.GASSH
2
```

```

3 3
10 10
.GASSPC
4 6
12 12
.MK2REF
0
.MK2DEL
12
.SYMMETRY
18g
.MAX MACRO
9
.MAX MICRO
4
.THRESH
1.0D-3
.DELETE
251..401
251..401
**END OF

```

C. Structure/basis set input file for DIRAC

```

INTGRL
Uranium dimer: Dyall's TZ basis
Linear symmetry, R(U-U)=2.53 Å
C 1 A
92. 2
U 1 0.00000000 0.00000000 0
U 2 0.00000000 0.00000000 -2.53
LARGE BASIS dyall.cv3z

```

FINISH

REFERENCES

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