

Relativistic Four-Component DFT Calculations of Vibrational Frequencies

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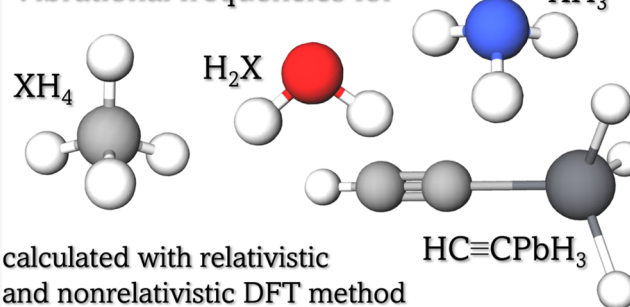
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Supporting Information

ABSTRACT: We investigate the effect of relativity on harmonic vibrational frequencies. Density functional theory (DFT) calculations using the four-component Dirac–Coulomb Hamiltonian have been performed for 15 hydrides (H_2X , $X = O, S, Se, Te, Po$; XH_3 , $X = N, P, As, Sb, Bi$; and XH_4 , $X = C, Si, Ge, Sn, Pb$) as well as for $HC\equiv CPbH_3$. The vibrational frequencies have been calculated using finite differences of the molecular energy with respect to geometrical distortions of the nuclei. The influences of the choice of basis set, exchange–correlation functional, and step length for the numerical differentiation on the calculated harmonic vibrational frequencies have been tested, and the method has been found to be numerically robust. Relativistic effects are noticeable for the heavier congeners H_2Te and H_2Po , SbH_3 and BiH_3 , and SnH_4 and PbH_4 and are much more pronounced for the vibrational modes with higher frequencies. Spin–orbit effects constitute a very small fraction of the total relativistic effects, except for H_2Te and H_2Po . For $HC\equiv CPbH_3$ we find that only the frequencies of the modes with large contributions from Pb displacements are significantly affected by relativity.

Vibrational frequencies for



INTRODUCTION

For molecules containing heavy atoms, relativistic effects play a crucial role in their electronic structure and chemical bonding.¹ Relativistic effects are commonly separated into scalar relativistic effects, which are due to (among other contributions) the mass–velocity and Darwin corrections, and the effects due to the spin–orbit interaction. The former lead for instance to contraction of the inner-shell orbitals (the energies of core levels are lower than those for the nonrelativistic case), and the latter result in the spin–orbit splitting of molecular orbital energy levels. Furthermore, the contraction of the inner-shell orbitals in turn increases the screening of the nuclear charge for the outer-shell electrons, giving rise to an indirect effect that results in expansion of the valence orbitals. These relativistic effects affect the valence orbitals involved with chemical bonding and consequently the potential energy surfaces.¹

In most cases where potential energy surfaces are concerned, it is sufficient to account for scalar relativistic effects using for example effective core potentials,² but for systems where strong spin–orbit effects may be expected, it is important to have an apparatus to calculate total relativistic effects using the four-component Dirac–Coulomb (or Dirac–Coulomb–Breit) Hamiltonian. Many four-component calculations have been carried out for dissociation energies^{1,3} and molecular gradients (first derivatives of the molecular energy with respect to distortions of the nuclei in the molecule)⁴ as well as equilibrium geometries.^{4,5} In this contribution, we present

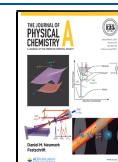
the results of calculations of the molecular Hessian (second derivatives of the molecular energy with respect to nuclear distortions) and harmonic vibrational frequencies with the Dirac–Coulomb Hamiltonian. Four-component methods for the analytic calculation of molecular Hessians (and thus also harmonic vibrational frequencies) are currently not available in any computational chemistry program package. Instead, our calculations have been carried out with an external driver to the existing program package DIRAC.⁶ Test calculations have been performed for hydrides of elements from groups 14 (XH_4 , $X = C, Si, Ge, Sn, Pb$), 15 (XH_3 , $X = N, P, As, Sb, Bi$), and 16 (H_2X , $X = O, S, Se, Te, Po$) and in addition for the acetylene derivative $HC\equiv CPbH_3$. Vibrational frequencies have been computed with the use of both relativistic and nonrelativistic methods in order to study the importance of the relativistic effects. Such calculations have previously been reported for halogen diatomics⁷ but not for polyatomic molecules.

There are well-established methods of calculating potential energy surfaces, including the molecular Hessian and vibra-

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tional frequencies, for molecular systems with substantial relativistic effects through the use of the zeroth-order regular approximation Hamiltonian,^{8,9} other two-component Hamiltonians,^{10–13} and relativistic effective core potentials.² In most cases these are sufficient for rendering the relativistic effects, apart from some systems with very strong spin–orbit coupling, such as some lanthanide compounds.^{1,14} However, a four-component protocol will be useful for benchmarking more approximate treatments of relativistic effects. We have recently also demonstrated that the geometry dependence of NMR spin–spin coupling constants depends more strongly on relativistic effects than the spin–spin coupling constants themselves.¹⁵ This suggests that relativity may be important for zero-point vibrational (ZPV) corrections to NMR properties. For properties such as spin–spin coupling constants, a full relativistic treatment is necessary, and it is therefore important also to develop tools that allow vibrational frequencies to be calculated at the full four-component level of theory.

METHODS

Numerical Derivatives. Our program works as an external driver to the DIRAC program package.⁶ The method for calculating the molecular Hessian and thus also the harmonic vibrational frequencies is fully numerical. Computation of the Hessian is based on calculating the second derivatives of the molecular energy with respect to geometric distortions of the molecule using simple three-point formulas:¹⁶

$$\frac{d^2E}{dx_\alpha^2} = \frac{E_{x_\alpha+h} - 2E_{x_\alpha} + E_{x_\alpha-h}}{h^2} \quad (1)$$

$$\frac{d^2E}{dx_\alpha dy_\beta} = \frac{E_{x_\alpha+h, y_\beta+h} - E_{x_\alpha-h, y_\beta+h} - E_{x_\alpha+h, y_\beta-h} + E_{x_\alpha-h, y_\beta-h}}{4h^2} \quad (2)$$

This means that the Hessian computation involves performing a number of energy calculations in which atoms are displaced from their original positions in all degrees of freedom. In the case of a molecule with N atoms, $18N^2 + 1$ single-energy computations need to be run to determine the full Hessian. Once the Hessian is obtained, the vibrational frequencies are calculated by diagonalization of the Hessian in its mass-weighted form.

When numerical differentiation is performed, it is important that an appropriate step length (h in the above equation) is used to ensure numerically accurate results. We performed test calculations of the vibrational frequencies for the water molecule with a number of different step lengths in the range of 10^{-1} – 10^{-5} Å. The calculations turned out to be numerically stable for step lengths between 10^{-2} – 10^{-4} Å. Similar test calculations for the H_2Po molecule revealed that in the case of heavier atoms, numerical stability shifts in the direction of larger step lengths (5×10^{-2} to 5×10^{-3} Å). All of the results can be found in the [Supporting Information](#). On this basis, in all of the subsequent calculations we used a step length of 10^{-3} Å. The only exceptions were systems involving the heaviest atoms (Pb, Bi, and Po), for which we used a step length of 10^{-2} Å. Using the differences between vibrational frequencies obtained with step lengths within the range of numerical stability, we were able to estimate the error bars to be about 3 cm^{-1} .

In order to test the numerical stability of the three-point formula, additional calculations were carried out using a five-point formula:¹⁶

$$\frac{d^2E}{dx_\alpha^2} = \frac{-E_{x_\alpha+2h} + 16E_{x_\alpha+h} - 30E_{x_\alpha} + 16E_{x_\alpha-h} - E_{x_\alpha-2h}}{12h^2} \quad (3)$$

No significant differences were found in comparison with the three-point formula with the same step length.

Geometry optimizations were performed using the DIRAC program⁶ at the same level of theory as for the Hessian calculations carried out afterward in order to ensure that the molecular gradient was equal to zero (a condition for the harmonic approximation). The convergence threshold for the gradient was 10^{-4} .

Single-Energy Calculations. The four-component Dirac–Kohn–Sham (DKS) energy calculations were carried out with the DIRAC program.⁶ The uncontracted aug-cc-pVDZ basis set¹⁷ on the hydrogen atoms and Dyall’s uncontracted triple- ζ basis set^{18–20} (dyall.v3z) on all of the other atoms were applied together with the B3LYP exchange–correlation functional,^{21–24} unless stated otherwise.

For comparison, four-component calculations with spin–orbit interactions switched off and nonrelativistic calculations were also carried out. In the case of the nonrelativistic computations, the speed of light was scaled to 2000.0 au in the Dirac–Coulomb Hamiltonian, and in the case of the four-component calculations without spin–orbit effects, the calculations were performed with Dyall’s spin-free Hamiltonian²⁵ as implemented in DIRAC.

Moreover, we carried out an investigation of the dependence of the results on the choice of exchange–correlation functional and basis set. In order to do so, four-component DKS calculations were performed using the PBE0 functional²⁶ (to be compared to B3LYP) and also two additional basis sets: (1) the uncontracted aug-cc-pVDZ basis set¹⁷ on the hydrogen atoms and Dyall’s uncontracted double- ζ basis set (dyall.v2z)^{19,20} on all of the other atoms and (2) the uncontracted aug-cc-pVQZ basis set¹⁷ on the hydrogen atoms and Dyall’s uncontracted quadrupole- ζ basis set (dyall.v4z)^{19,20} on all of the other atoms.

The convergence threshold for all of the single-energy calculations was 10^{-6} .

Since an analytical method for calculating the molecular Hessian is implemented in the DALTON program,^{27,28} some calculations were performed with this program for comparison. We note that DALTON allows only one-component nonrelativistic DFT calculations. All of the DALTON computations were run with the same uncontracted basis set and exchange–correlation functional as above and were carried out using the geometry optimized in DIRAC at the nonrelativistic level of theory (the same geometry as the one used for nonrelativistic numerical calculations of vibrational frequencies).

RESULTS AND DISCUSSION

In order to test the newly developed method for calculating harmonic vibrational frequencies, simple systems consisting of three, four, or five atoms have been chosen:

- H_2X where $X = O, S, Se, Te, Po$;
- XH_3 where $X = N, P, As, Sb, Bi$;
- XH_4 where $X = C, Si, Sn, Pb$.

In addition to this, to illustrate the usefulness of the presented method for a larger system, we have calculated vibrational frequencies for an acetylene derivative, $\text{HC}\equiv\text{CPbH}_3$.

Influences of the Basis Set and Exchange–Correlation Functional on the Vibrational Frequencies. The results of four-component DFT calculations employing either the B3LYP or PBE0 functional for the vibrational frequencies of H_2X (X = O, S, Se, Te, Po) can be found in Table 1. In most

Table 1. Vibrational Frequencies for H_2X : Comparison of Results Calculated with Either the B3LYP or PBE0 Functional^a

X	functional	ω_1 [cm^{-1}]	ω_2 [cm^{-1}]	ω_3 [cm^{-1}]
O	B3LYP	3918	3815	1623
	PBE0	3983	3877	1630
S	B3LYP	2686	2671	1206
	PBE0	2730	2714	1199
Se	B3LYP	2401	2388	1061
	PBE0	2448	2434	1059
Te	B3LYP	2109	2102	885
	PBE0	2152	2144	885
Po	B3LYP	1846	1829	777
	PBE0	1901	1885	778

^aFour-component DKS Hamiltonian with the indicated functional and the aug-cc-pVTZ (on H) + dyall.v3z (on X) basis set.

cases the frequencies obtained with PBE0 are larger, but the differences between the results obtained with PBE0 and B3LYP do not exceed 3% in any case. Taking this into consideration, it seems that in this case B3LYP and PBE0 would produce comparable results. The B3LYP functional has been chosen for the following calculations because of its good performance for vibrational properties reported in the literature.^{29–31}

The results of the four-component DFT calculations of vibrational frequencies for H_2X systems, carried out with double- ζ , triple- ζ , and quadruple- ζ quality basis sets, can be found in Table 2. The differences between vibrational

Table 2. Vibrational Frequencies for H_2X : Comparison of Results Calculated with Three Different Basis Sets^a

X	basis set	ω_1 [cm^{-1}]	ω_2 [cm^{-1}]	ω_3 [cm^{-1}]
O	DZ ^b	3887	3787	1630
	TZ ^c	3918	3815	1623
	QZ ^d	3918	3816	1626
S	DZ ^b	2680	2666	1196
	TZ ^c	2686	2671	1206
	QZ ^d	2688	2675	1208
Se	DZ ^b	2408	2393	1059
	TZ ^c	2401	2388	1061
	QZ ^d	2407	2394	1060
Te	DZ ^b	2114	2107	890
	TZ ^c	2109	2102	885
	QZ ^d	2117	2110	885
Po	DZ ^b	1844	1827	777
	TZ ^c	1846	1829	777
	QZ ^d	1848	1832	778

^aFour-component DKS Hamiltonian with the B3LYP functional and the indicated basis set. ^baug-cc-pVDZ (on H) + dyall.v2z (on X). ^caug-cc-pVTZ (on H) + dyall.v3z (on X). ^daug-cc-pVQZ (on H) + dyall.v4z (on X).

frequencies obtained with these three basis sets are almost negligible. The biggest differences occur between DZ and QZ for the H_2O molecule, yet even in this case these differences are not larger than 1% of the values, being at most 31 cm^{-1} . In all other cases, the differences do not exceed 10 cm^{-1} . In light of the above findings, the triple- ζ -quality basis set appears to be an optimal compromise between accuracy and computational cost, and this basis set has been used in all of the following calculations.

Numerical versus Analytical Hessian. As numerical methods for calculating the molecular Hessian will inevitably have limitations on the numerical accuracy, we have tried to estimate these by comparing the numerical harmonic vibrational frequencies with the results obtained with the analytical nonrelativistic method implemented in the DALTON program. The comparison of the calculated harmonic vibrational frequencies can be found in Table 3. We obtained excellent agreement in case of the H_2O , H_2S and H_2Se molecules.

Table 3. Vibrational Frequencies for H_2X : Comparison of Results Calculated with Relativistic and Nonrelativistic DFT Methods^a

X	method ^b	ω_1 [cm^{-1}]	ω_2 [cm^{-1}]	ω_3 [cm^{-1}]	
		(A ₁ symmetry, X–H symmetric stretch)	(B ₂ symmetry, X–H asymmetric stretch)	(A ₁ symmetry, H–X–H bend)	
O	num rel	3918	3815	1623	
		no SO	3902	3799	1627
	anal nrel	nrel	3920	3817	1623
		experimental ³²	3920	3818	1623
		experimental ³²	3756	3657	1595
S	num rel	2686	2671	1206	
		no SO	2685	2671	1205
	anal nrel	nrel	2690	2676	1204
		experimental ³²	2690	2676	1205
		experimental ³²	2626	2615	1183
Se	num rel	2401	2388	1061	
		no SO	2404	2390	1061
	anal nrel	nrel	2416	2404	1058
		experimental ³²	2418	2406	1059
		experimental ³²	2358	2345	1034
Te	num rel	2109	2102	885	
		no SO	2122	2115	888
	anal nrel	nrel	2147	2142	884
		experimental ³³	2147	2142	885
		experimental ³³	2072	2065	861
Po	num rel	1845	1828	775	
		no SO	1977	1972	812
	anal nrel	nrel	2032	2031	806
		2032	2030	809	

^aB3LYP functional, aug-cc-pVTZ (on H) + dyall.v3z (on X) basis set.

^bFundamental vibrational frequencies are reported for the experimental data. For the calculated results, the following notation is used: num, numerical; anal, analytic; rel, relativistic; nrel, nonrelativistic; no SO, no spin–orbit coupling.

Influence of Relativity on the Vibrational Frequencies. Harmonic vibrational frequencies calculated with the relativistic and nonrelativistic methods are summarized in Tables 3 – 5. As can be noted, in almost all cases the relativistic vibrational frequencies are smaller than the corresponding nonrelativistic values, that is, relativity decreases

Table 4. Vibrational Frequencies for XH₃: Comparison of Results Calculated with Relativistic and Nonrelativistic DFT Methods^a

X	method ^c	ω_1 [cm ⁻¹] (A ₁ symmetry, X–H symmetric stretch)	ω_2 [cm ⁻¹] (E symmetry, X–H asymmetric stretch) ^b	ω_3 [cm ⁻¹] (E symmetry, H–X–H scissor) ^b	ω_4 [cm ⁻¹] (A ₁ symmetry, X–H wag)
N	rel	3596	3476	1661	1019
	no SO	3584	3465	1663	1029
	nrel	3587	3467	1662	1024
	experimental ³²	3444	3337	1627	950
P	rel	2385	2374	1136	1016
	no SO	2385	2375	1136	1016
	nrel	2389	2379	1136	1024
	experimental ³²	2328	2323	1118	992
As	rel	2168	2154	1016	937
	no SO	2168	2154	1017	937
	nrel	2183	2171	1016	930
	experimental ³²	2123	2116	1003	906
Sb	rel	1933	1926	844	812
	no SO	1933	1926	842	809
	nrel	1961	1958	842	803
	experimental ³⁴	1894	1891	831	782
Bi	rel	1768	1766	764	750
	no SO	1796	1788	773	760
	nrel	1855	1852	765	742
	experimental ³⁴	1734	1733	751	726

^aB3LYP functional, aug-cc-pVTZ (on H) + dyall.v3z (on X) basis set. ^bNo symmetry has been used, so frequencies of degenerate vibrations vary (by at most 2 cm⁻¹). Arithmetic averages are given. ^cFundamental vibrational frequencies are reported for the experimental data. For the calculated results, the following notation is used: rel, relativistic; nrel, nonrelativistic; no SO, no spin–orbit coupling.

Table 5. Vibrational Frequencies for XH₄: Comparison of Results Calculated with Relativistic and Nonrelativistic DFT Methods^a

X	method ^c	ω_1 [cm ⁻¹] (A ₁ symmetry, X–H symmetric stretch)	ω_2 [cm ⁻¹] (T ₂ symmetry, X–H asymmetric stretch) ^b	ω_3 [cm ⁻¹] (E symmetry, H–X–H twist) ^b	ω_4 [cm ⁻¹] (T ₂ symmetry, H–X–H scissor) ^b
C	rel	3135	3032	1555	1337
	no SO	3127	3025	1557	1339
	nrel	3127	3025	1556	1339
	experimental ³²	3019	2917	1534	1306
Si	rel	2237	2227	977	918
	no SO	2237	2227	977	918
	nrel	2238	2228	976	917
	experimental ³²	2191	2187	975	914
Ge	rel	2144	2136	934	827
	no SO	2143	2136	932	826
	nrel	2144	2139	925	823
	experimental ³²	2114	2106	931	819
Sn	rel	1929	1927	753	686
	no SO	1930	1927	752	684
	nrel	1930	1926	737	678
Pb	rel	1839	1827	686	609
	no SO	1847	1823	693	616
	nrel	1847	1839	664	609

^aB3LYP functional, aug-cc-pVTZ (on H) + dyall.v3z (on X) basis set. ^bNo symmetry has been used, so frequencies of degenerate vibrations vary (by at most 2 cm⁻¹). Arithmetic averages are given. ^cFundamental vibrational frequencies are reported for the experimental data. For the calculated results, the following notation is used: rel, relativistic; nrel, nonrelativistic; no SO, no spin–orbit coupling.

the bond strength. In the case of the H₂X systems, relativistic effects are significant for H₂Te (2% for ω_1 and ω_2) and H₂Po (10% for ω_1 and ω_2 , 3% for ω_3). Also in the case of the XH₃ molecules, relativistic effects are not negligible for the two heaviest congeners, 2% for ω_1 and ω_2 in SbH₃ and 8% for ω_1 , 5% for ω_2 , and 2% for ω_3 in BiH₃. In the case of the XH₄ molecules, relativistic effects are negligible for all but one mode, ω_3 (E symmetry mode), for SnH₄ (2%) and PbH₄ (6%).

It should be stressed here that the percentage change in the values when calculated with relativistic and nonrelativistic methods varies for each vibrational mode.

In addition, for all of the molecules, relativistic four-component calculations without spin–orbit effects have been performed (Table 4). These results show that in the case of XH₃, all of the relativistic effects are in fact scalar relativistic effects, whereas in the case of H₂X, spin–orbit effects play a

crucial role. Spin–orbit effects constitute about 30% of the relativistic effects in the case of H₂Te and as much as 70% in the case of H₂Po.

Comparison with Experimental Values. When comparing the results obtained with the experimental values, one should keep in mind that the diagonalization of the molecular Hessian gives us harmonic vibrational frequencies. Thus, anharmonicity is not taken into account, and this will lead to some difference between the results and the experimental values. In our case, the differences do not exceed 5%, in line with the expected magnitude of anharmonic corrections.³⁵

Vibrational Frequencies for HC≡CPbH₃. To illustrate the usefulness of the presented method and to study the effects of relativity on vibrational frequencies for a more complex system where only some of the modes involve the heavy atom, we have calculated the vibrational frequencies for the acetylene derivative HC≡CPbH₃ with both relativistic and nonrelativistic approaches. The motivation for choosing this particular system was our previous work,¹⁵ where we showed that for this molecule the relativistic effects on the derivatives of the indirect spin–spin coupling constants with respect to molecular geometry parameters tend to be more pronounced than the effects on the coupling constants themselves. The ZPV corrections calculated at the nonrelativistic level are therefore not necessarily reliable. The uncontracted aug-cc-pVDZ basis set¹⁷ was used on the hydrogen and carbon atoms and Dyal's uncontracted triple- ζ basis set (dyall.v3z)^{18–20} on the lead atom have been applied together with the B3LYP exchange–correlation functional.^{21–24} The results are collected in Table 6.

Table 6. Vibrational Frequencies for HC≡CPbH₃: Comparison of Results Calculated with Relativistic and Nonrelativistic DFT Methods^a

mode	relativistic [cm ⁻¹]	nonrelativistic [cm ⁻¹]
C–H stretch (A ₁ symmetry)	3445	3440
C–C stretch (A ₁ symmetry)	2117	2116
Pb–H asymmetric stretch (E symmetry) ^b	1857	1840
Pb–H symmetric stretch (A ₁ symmetry)	1846	1846
C–C–H bend (A ₂ symmetry) ^b	708	702
H–Pb–H wag (A ₁ symmetry)	621	613
H–Pb–H scissor (E symmetry) ^b	641	597
H–C–C–Pb wag (A ₂ symmetry) ^b	482	429
C–Pb stretch (A ₁ symmetry)	384	409
C–C–Pb bend (A ₂ symmetry) ^b	187	145

^aB3LYP functional, aug-cc-pVTZ (on H and C) + dyall.v3z (on Pb) basis set. ^bNo symmetry has been used, so frequencies of degenerate vibrations vary (by at most 5 cm⁻¹). Arithmetic averages are given.

In the case of the HC≡CPbH₃ molecule, it seems that only vibrations that involve the Pb atom are significantly affected by relativity. There is almost no difference between the relativistic and nonrelativistic values of vibrational frequencies for C–H stretching, C–C stretching, and C–C–H bending. This finding may be useful for future calculations of vibrational effects on molecular properties for large molecules, since it may allow for relativity to be taken into account only for selected localized modes. Similar findings were previously reported by Berger et al.³⁶ In addition to this, the relativistic effects are much more pronounced for deformation modes than for

stretching modes. The difference between the vibrational frequencies calculated with relativistic and nonrelativistic methods for the C–C–Pb bend exceeds 20% of the value, whereas for the C–Pb stretch it is only little more than 5%.

CONCLUSIONS

We have presented a numerical method for calculating the molecular Hessian and harmonic vibrational frequencies with relativistic four-component DFT. Test calculations have been performed for hydrides of elements from groups 14, 15, and 16. We have achieved good agreement with an analytical nonrelativistic DFT method.

Relativistic effects become significant primarily for the hydrides containing atoms from the fifth and sixth rows of the periodic table and are much more pronounced for the vibrational modes with higher frequencies. Spin–orbit effects constitute a very small fraction of the relativistic effects on the whole, with the exception of H₂Te and H₂Po. Additional calculations for HC≡CPbH₃ show that only the frequencies of the modes with large contributions from Pb displacements are significantly affected by relativity.

This work is considered a stepping stone towards the development of a four-component relativistic numerical method for calculating ZPV corrections to NMR parameters (spin–spin coupling constants and shielding constants).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpca.1c07398>.

Vibrational frequencies for H₂O and H₂Po obtained with different step lengths and different optimized geometries (PDF)

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Notes

The authors declare no competing financial interest.

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