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Comment on “Going beyond the frozen core approximation: Development of coordinate-dependent pseudopotentials and application to Na_2^+ ” [J. Chem. Phys. 138, 054110 (2013)]

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The recent paper by Kahros and Schwartz, “Going beyond the frozen core approximation: Development of coordinate-dependent pseudopotentials and application to Na_2^+ ,”¹ contains important omissions and inconsistencies, therefore we feel obliged to draw attention to the following points:

- (i) In their motivating central assumption that “all pseudopotentials, whether developed exactly or empirically, are subject to the frozen core approximation (FCA)” Kahros and Schwartz (KSCh) fail to notice the progress achieved in pseudopotentials some 30 years ago. Up to the early 1980s the FCA has been a stumbling block and an unresolved dilemma in the development of reliable pseudopotentials, which needed an additional basic anchor in quantum theory. The FCA generally causes deviations in bond energies and distances, in particular for molecules containing highly polarizable atomic cores, e.g., K_2^+ , or K_2 .^{2–4} Subsequently, however, coordinate dependent pseudopotentials have been properly introduced and successfully demonstrated precisely on Na_2^+ and K_2^+ along with other molecular ions.^{2,3}

The basic tool in generating coordinate dependent pseudopotentials has been provided by the core-polarization potential (CPP), $V_{pol}(\mathbf{r}, \mathbf{R})$, introduced in the seminal work of Meyer and co-workers.^{4,5} Here \mathbf{r} and \mathbf{R} represent the electronic and the nuclear coordinates, respectively. The appropriate $V_{pol}(\mathbf{r}, \mathbf{R})$ may be incorporated into any pseudopotential, whether semiempirical or not. For pseudopotentials the inclusion of CPPs not only corrects for the FCA errors at the Hartree-Fock (HF) level but also accounts for the core-valence correlation.^{2,3,6–10} The CPPs do not require molecular fitting; they use transferable parameters based on atomic data (experimental or *ab initio* ones) and describe non-frozen-core effects in a physically well motivated coordinate-dependent form. Early applications yielded a high-accuracy description of non-frozen-core effects, for instance, in alkali and coinage metal dimers, their hy-

drides, and their cations.^{2–4,6,8} In addition, atomic properties incorrectly described within the FCA were accurately calculated, as first shown for the dipole polarizabilities of alkali, coinage metal, and alkaline-earth atoms.^{5,7} Subsequently, the coupling of the CPPs with atom-adjusted frozen-core pseudopotentials has been amply reported and reviewed in the literature of the last 30 years.^{9–13}

- (ii) The new results for Na_2^+ by KSCh are definitely inferior to the above-mentioned older results, since the core-valence correlation effects included in the older work are not considered in their HF treatment. KSCh claim that their “method completely takes into account polarization effects on the core molecular orbitals and how these effects change with a change in the nuclear coordinates.”¹ This claim, however, cannot be upheld. Specifically for Na_2^+ , the contracting effect on the valence orbital due to the dynamic polarization of the cores is mainly responsible for the bond-length reduction beyond FCA.⁴ It is much larger than the HF frozen-core error, which is exclusively treated by KSCh. For HF calculations on Na_2^+ the replacement of the fully optimized cores by frozen cores from free Na^+ ions increases the bond-length by less than 0.01 Å only. On the other hand, the neglect of core-valence correlation leads to a calculated bond length that is too large by 0.12 Å.^{2,4}
- (iii) Unfortunately, the new results for Na_2^+ by KSCh do not even qualify as estimates of the non-frozen-core effects at the HF level. To support this statement let us consider two properties discussed in Ref. 1, viz., the bond-length and the vibrational frequency. The HF frozen-core bond-length error of 0.3 Å (8%) for Na_2^+ reported in their paper is more than an order of magnitude larger than the one obtained in HF all-electron calculations with atomically frozen cores (0.01 Å, see above). From Fig. 4 of Ref. 1 it becomes apparent that the problem lies with the superposition of atomic FCA pseudopotentials. Note, however, that this is no indication for an error of the superposition of atom-adjusted pseudopotentials in general. For instance, superposing the FCA pseudopotentials of Ref. 2 reproduces the all-electron frozen-core bond length of Na_2^+ to 0.01 Å, and similar results are obtained with

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standard norm-conserving pseudopotentials available in literature.

If coupled with a decrease of bond energy, an increase in bond-length normally results in a decreased vibrational frequency. Surprisingly, KSch report and defend an almost 10% increase in their FCA vibrational frequency as compared to their full HF value. According to KSch this was to be “expected given that the FCA overestimates the attraction of electrons to the center of the molecular bond.”¹ High quality all-electron HF calculations compared to the corresponding FCA results show, however, that the vibrational frequency is practically unaffected on the respective levels of theory. Therefore, the reported 10% increase in frequency appears to be an artifact.^{14,15} Altogether KSch obtain FCA shifts in bond dissociation energy, bond-length, and vibrational frequency that disagree with those of other calculations, and appear to lack internal consistency.^{14,15}

The reasons for the failures of a FCA type superposition of the atomic Phillips-Kleinman (PK) pseudopotentials¹⁶ for molecular Na_2^+ are not entirely clear so far. KSch transform their pseudopotentials into a local form, independent of the angular momentum. Although large errors are well known to arise by using such local pseudopotentials in general, they work relatively well for Na. However, problems might arise from using finite basis sets for the pointwise determination of the local pseudopotentials, as mentioned by KSch in Ref. 1. Additional problems may be caused by their use of non-norm-conserving PK pseudo-orbitals, whose valence densities are reduced with respect to the all-electron case. The concomitant errors are well documented in the literature for the many-electron case.^{17,18} In the one-valence-electron case, the long-range bonding will be weakened if the atomic pseudo-orbital tails decay too fast. The general point is, however, that the above failures are hardly, if at all, connected to the coordinate-dependent molecular changes of the Na core orbitals.

Summarizing our comments here, the new method of KSch is unfortunately hampered by inconsistencies. Neglecting previous work on core-polarization potentials, the KSch pseudopotential treatment of non-frozen-core effects suffers

from partial error compensation between gross overestimation at the HF level and neglect of core-valence correlation. At the HF level, the inaccuracies of the order of 10%, attributed to the frozen-core approximation by KSch, seem to be mainly due to superposing non-norm-conserving atomic pseudopotentials. In fact, the HF potential-energy curve of Na_2^+ is satisfactorily (to <1%) reproduced both at the frozen-core all-electron HF level and with frozen-core norm-conserving pseudopotentials without any molecular adjustment. By construction, the new coordinate-dependent KSch pseudopotential for Na_2^+ also reproduces the all-electron HF potential-energy curve for Na_2^+ . However, the tails of the density of the valence orbital are still reduced with respect to the all-electron case. Therefore, similar norm conservation errors, as here documented for the atomic KSch pseudopotentials, are likely to arise with the new coordinate-dependent KSch pseudopotential in applications to other systems/states than just the ground-state potential-energy curve of gas-phase Na_2^+ .

¹A. Kahros and B. J. Schwartz, *J. Chem. Phys.* **138**, 054110 (2013).

²P. Fuentealba, H. Preuss, H. Stoll, and L. von Szentpály, *Chem. Phys. Lett.* **89**, 418 (1982).

³L. von Szentpály, P. Fuentealba, H. Preuss, and H. Stoll, *Chem. Phys. Lett.* **93**, 555 (1982).

⁴W. Müller and W. Meyer, *J. Chem. Phys.* **80**, 3311 (1984).

⁵W. Müller, J. Flesch, and W. Meyer, *J. Chem. Phys.* **80**, 3297 (1984).

⁶H. Stoll, P. Fuentealba, M. Dolg, J. Flad, L. von Szentpály, and H. Preuss, *J. Chem. Phys.* **79**, 5532 (1983).

⁷P. Fuentealba, *J. Phys. B* **15**, L555 (1982); P. Fuentealba, H. Stoll, L. von Szentpály, P. Schwerdtfeger, and H. Preuss, *ibid.* **16**, L323 (1983); P. Fuentealba, L. von Szentpály, H. Preuss, and H. Stoll, *ibid.* **18**, 1287 (1985).

⁸G. Igel-Mann, U. Wedig, P. Fuentealba, and H. Stoll, *J. Chem. Phys.* **84**, 5007 (1986).

⁹A. Nicklass and H. Stoll, *Mol. Phys.* **86**, 317 (1995).

¹⁰A. Nicklass and K. A. Peterson, *Theor. Chem. Acc.* **100**, 103 (1998).

¹¹P. Pyykkö and H. Stoll, *Relativistic Pseudopotential Calculations, Specialist Periodical Reports, Chemical Modelling, Applications and Theory, Vol. 1*, edited by A. Hinchliffe (R.S.C., Cambridge, UK, 2000).

¹²P. Schwerdtfeger, *ChemPhysChem* **12**, 3143 (2011).

¹³M. Dolg and X. Cao, *Chem. Rev.* **112**, 403 (2012).

¹⁴In an Erratum¹⁵ KSch have now corrected the vibrational frequencies, which apparently have been switched in the original paper.

¹⁵A. Kahros and B. J. Schwartz, *J. Chem. Phys.* **139**, 149901 (2013).

¹⁶J. C. Phillips and L. Kleinman, *Phys. Rev.* **116**, 287 (1959).

¹⁷P. Durand and J.-C. Barthelat, *Theor. Chim. Acta* **38**, 283 (1975); J.-C. Barthelat, P. Durand, and A. Serafini, *Mol. Phys.* **33**, 159 (1977).

¹⁸P. A. Christiansen, Y. S. Lee, and K. S. Pitzer, *J. Chem. Phys.* **71**, 4445 (1979).