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Response to "Comment on 'Going beyond the frozen core approximation: Development of coordinate-dependent pseudopotentials and application to Na_2^+'" [J. Chem. Phys. 139, 147101 (2013)]

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In condensed-phase mixed quantum/classical (MQC) molecular dynamics (MD) simulations,[1–3] the potentials employed are typically subject to the frozen core approximation (FCA). Such potentials are usually derived for an isolated molecule in the gas phase, and if the molecule's nuclear or electronic coordinates change upon entering a complex environment, the calculated MQC dynamics could be highly inaccurate because the potential cannot respond to the interactions with the solvent. In our original paper,[4] we presented a general method to go beyond the FCA in MQC MD simulations through the rigorous calculation of exact pseudopotentials that can respond dynamically to changes in a solute's molecular coordinates. To illustrate the use of our method, we applied it to the sodium dimer cation molecule. We began with rigorously calculated, non-norm-conserving, unoptimized atomic pseudopotentials based on the Phillips-Kleinman (PK) formalism[5–8] for each of the molecule's two sodium cation cores, and showed that our method provides a means to calculate a corrective function that allows for the construction of an exact, dynamical, norm-conserving molecular pseudopotential that includes polarization effects at the Hartree-Fock (HF) level. Our choice to begin with the sodium dimer cation system stemmed from the fact that there is negligible discrepancy between the calculated energies for the LUMO of Na_2^{2+} and the HOMO of Na_2^+ (Fig. 4 of our original paper). This allowed us to conclude that Koopmans' theorem[9] is valid for this molecule so that we could focus our efforts on using our method to incorporate the effects of core-core polarization and correcting for norm-non-conservation while reasonably neglecting the effects of core-valence polarization. The result is that for a given choice of basis set, our method produced a coordinate-dependent pseudopotential, which when used in a one-electron calculation, provided an electronic structure that is equivalent to a full HF calculation at internuclear separations from bonding to the dissociation limit for this molecule.

In their Comment on our paper, Stoll, Fuentealba, and Szentpály (SFS) first argue that our potential for Na_2^+ is inferior compared to other potentials developed for this molecule,[12–15] due to the fact that we have neglected dynamic (valence) polarization.[10] Since dynamic polarization is a post-HF effect and our method is designed to reproduce all-electron quantum mechanical calculations in the static exchange approximation, we cannot account for such effects, and it is clear from our formalism that we never claimed to do so. Thus, we fully agree that potentials that were specifically crafted with atom-adjusted parameters tuned to the results of experimental observations and/or high level quantum chemistry calculations are superior to ours at describing the behavior of the gas-phase Na_2^+ molecule. Our goal was to present a general method, applicable to any system, for the creation of exact, dynamical molecular pseudopotentials that are able to fully reproduce all-electron Hartree-Fock calculations in condensed phases without introducing empiricism. For example, it is straightforward to extend the application of our method to include the effects of the position of a nearby solvent molecule or changes in bond angle on a solute molecule's core orbitals. The application of our formalism to Na_2^+ and the creation of a dynamic pseudopotential for this molecule, parameterized by the internuclear separation of the molecule's constituent atoms, served as an illustration of the usage of our method and a guide to how it can be applied in practice. Thus, our coordinate-dependent pseudopotential should not be viewed as a replacement for the potentials developed by Stoll and co-workers[14,15] for this system. In fact, one could easily add the core polarization potentials (CPP) developed specifically for sodium dimer cation by Meyer and Fuentealba[12,13] to our coordinate-dependent pseudopotential to capture post-HF core-valence, dynamic polarization effects for this particular molecule.

Next, SFS state in their Comment that we have overestimated the effects of core-core polarization for the Na_2^+ molecule.[10] In the application of our method to the sodium dimer cation, we made a sign error in the expression for the basis set with which we calculated the molecular pseudo-orbital and thus the corresponding pseudopotential; this error required us to re-calculate the coordinate-dependent pseudopotential for sodium dimer cation.[11] As a result of the error, the calculations specific to Na_2^+ in our original paper overestimated the effects of core-core polarization, giving an incorrect picture for the charge density of the molecule's bonding electron (Fig. 5 of Ref. 4). The error did not affect any of the original calculations related to the "frozen core" (i.e., unoptimized atomic) potentials and so the FCA that results from the superposition of these potentials for the sodium dimer cation molecule remain unaffected. When the error is corrected (see Fig. 5 of Ref. 11), we find a much greater resemblance between the HF molecular orbital and the superposition of the

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"frozen core" atomic potentials that we implemented (which were based on previous work[8]), indicating less pronounced core-core polarization effects than we had previously stated. Importantly, however, our error caused no change in the potential energy curve we calculated (Fig. 4 of the original paper), nor in the molecule's equilibrium bond length, dissociation energy, or vibrational frequency.[11] This is because the PK formalism upon which our method is based guarantees that one retrieves the eigenenergy specified by an electronic structure calculation and the pseudo-orbital from which the implemented pseudopotential was calculated. Thus, the mathematical error we made provided an incorrect expression for the molecule's pseudo-orbital but did not affect the calculated eigenenergy. We thank SFS for providing us with the opportunity to discover and correct our error, but we note that although the aforementioned error did cause us to overestimate the effects of core-core polarization for this particular molecule, the error does not affect the generality of our method, only the particular application to the Na_2^+ molecule (which has now been corrected[11]).

Finally, SFS also claim that our potential does not provide a significantly better description of the Na_2^+ molecule than a simple Na atomic pseudopotential superposition.[10] In particular, they point out that the superposition of the atomic potentials developed by Fuentealba[15] yields satisfactory results and only increases the equilibrium bond length by 0.01 Å. Again, however, we note that these atomic pseudopotentials include empirically adjusted parameters, while our "frozen core" atomic potentials were rigorously derived from the PK formalism in a manner general to any atom and/or molecule, and thus were in no way optimized. Additionally, our "frozen core" potentials were non-norm-conserving and our corrective function also needed to account for this lack of norm conservation. Thus, our method provides a means to correctly reproduce the potential energy curve obtained via an all-electron Hartree-Fock calculation with a one-electron coordinate-dependent pseudopotential based on unoptimized, non-norm-conserving atomic potentials without using a single adjustable parameter.[4] This was precisely the aim of our work. SFS go on to state that our approach is problematic precisely because it is based on unoptimized non-norm-conserving[16] "frozen core" atomic potentials.[10] Of course, the use of unoptimized atomic potentials leads to errors when calculating molecular properties because of the lack of norm conservation, and this is precisely what we referred to in our original paper as the FCA limit and why we see a discrepancy between the molecular properties obtained from a superposition of our "frozen core" atomic potentials and those we calculated using our coordinate-dependent formalism for the sodium dimer cation. The corrective function calculated with our method, therefore, corrects any problems caused by the lack of norm-conservation by reproducing the molecule's exact pseudo-orbital at every internuclear separation. Thus, our method is capable of using generic, unoptimized, non-norm-conserving potentials in the construction of coordinate-dependent potentials that are effectively norm-conserving. This is why our method can reproduce an all-electron HF calculation at all internuclear separations—for any molecule—without the need for tuning or adjustable parameters.

In conclusion, the majority of the comments by SFS seem to be the result of a misunderstanding of the purpose of our work, in that our aim was to present a general method at the Hartree-Fock level of theory for creating exact dynamical potentials starting with unoptimized atomic potentials; we never proposed to replace the accurate CPPs developed specifically for the system to which we applied our method as a proof of principle. SFS are indeed correct in that the particular application of our method to the Na_2^+ molecule overestimated core-core polarization due to an error, which now has been fully corrected.[11] The fact that our method can be successfully applied to molecules like sodium dimer cation shows that our method is robust and generally applicable to any molecule. Thus, nothing in the SFS Comment affects the method that we present in our work or its significance and, in fact, the formalism underlying our method, which unambiguously provides for the construction of exact, dynamical pseudopotentials within the Hartree-Fock framework for use in MQC MD simulations, has not been called into question.

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