Erratum: “Going beyond the frozen core approximation: Development of coordinate-dependent pseudopotentials and application to Na$_2^+$”  

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In our original paper,$^1$ we presented a method for the development of coordinate-dependent pseudopotentials that was designed to reproduce all-electron quantum chemistry calculations of Hartree-Fock (HF) quality from bonding to complete dissociation. Our method is based on the Phillips-Kleinman formalism (PK),$^2$ and as such, can be straightforwardly applied to any chemical system, and we anticipate many applications for this formalism in condensed-phase simulations. As a proof of principle, we applied our technique to the sodium dimer cation molecule, Na$_2^+$. Unfortunately, after publication of our paper, we discovered a sign error in our expression for the basis set used to calculate the molecule’s pseudo-orbital and thus its corresponding pseudopotential. This error affected all of the figures and the table in our original manuscript as well as the functional form chosen to represent the pseudopotential, since each of these pertains to the specific way we generated the coordinate-dependent pseudopotential. The key consequence of our basis set coding error was that our original, incorrectly expressed pseudo-orbital and thus its corresponding pseudopotential. This error affected all of the figures and the table in our original manuscript as well as the functional form chosen to represent the pseudopotential, since each of these pertains to the specific way we generated the coordinate-dependent pseudopotential. This error affected all of the figures and the table in our original manuscript as well as the functional form chosen to represent the pseudopotential, since each of these pertains to the specific way we generated the coordinate-dependent pseudopotential.

The key consequence of our basis set coding error was an overestimation of the effects of core-core polarization for the Na$_2^+$ molecule, as was pointed out in the Comment on our work by Stoll and co-workers.$^3$ This was a result of the fact that our original, incorrectly expressed pseudo-orbital yielded a pseudopotential for this molecule that overly repelled electrons from the molecule’s center of mass (COM) and overly attracted them to the regions near the Na atoms outside the bonding axis. When we repeat the calculation (as outlined in Sec. III A of our original manuscript) and correct the error, we still find that the implementation of “frozen core approximation” (FCA) atomic potentials leads to an overbinding of the valence electron at the molecule’s COM as compared to all-electron HF calculations. However, the results in our original paper overestimate this effect by roughly an order of magnitude. As described in our original manuscript, the FCA atomic potentials we implemented were non-norm-conserving PK pseudopotentials for each of the Na$^+$ cores, calculated previously by Smallwood and co-workers,$^4$ we also chose the same basis set as Smallwood and co-workers for the construction of the Na$_2^+$ molecular pseudopotential both in our original manuscript and in this Erratum. With the basis set sign error fixed, the correct results for Na$_2^+$ can be seen in Figure 1, where we plot two-dimensional cross-sections of $U^{Na^+_2}(r_1, r_2; R)$, $U^{Na^+_2}(r_1) + U^{Na^+_2}(r_2)$, and $\xi(r_1, r_2; R)$ (as defined in Eqs. (8)–(10) of our original manuscript$^1$), where the cross-sections shown are taken through the internuclear bonding axis at $R = 3.7 \, \text{Å}$, the HF-calculated equilibrium bond distance of Na$_2^+$ with our chosen basis set. Since only the calculations related to the molecular pseudopotential were affected by our mathematical error, Figure 1(b) is identical to that in our original manuscript, while the corrected molecular pseudopotential is reflected in Fig. 1(a) in this Erratum and in the difference between these potentials, Fig. 1(c).

We then carried out the same procedure in our original work of fitting the numerically calculated $\xi(r_1, r_2; R)$ functions at a number of internuclear distances to an analytic function.$^1$ The new functional form we chose was

$$
\xi_{\text{fit}}(r_1, r_2; R) = b[e^{-c_1r_1} + e^{-c_2r_1}] + f\left[r_1^2e^{-2c_1r_1} + r_2^2e^{-2c_2r_2}\right] + h[e^{-x_1r_1} + e^{-x_2r_1}] + i[e^{-y_1r_1} + e^{-y_2r_1}]
$$

$$
+ l\left[r_1^2e^{-2x_1r_1} + r_2^2e^{-2x_2r_2}\right] + m\left[r_1^2e^{-2y_1r_1} + r_2^2e^{-2y_2r_1}\right] + i e^{-j_1r_1},
$$

(1)

which consists of identical atom-centered Gaussian and $e^{-c}r$ functions, one $e^{-c}r$ function at the molecule’s COM, and identical Gaussian and $e^{-c}r$ functions at the mid-point of the COM and each of the atomic sites (denoted by the subscripts 1cm and 2cm in Eq. (1)). This function contains ten fitting parameters, $b(R) - j(R)$, and Figure 2 shows a fit of $\xi(r_1, r_2; R)$ with the above function at a representative inter-nuclear distance. As done previously,$^1$ we then interpolated the pseudopotential by fitting the fitting parameters of Eq. (1) to rational polynomials of various degrees in $R$. As in our original manuscript, the fitting parameters behave smoothly, yielding a continuous, nested expression for our coordinate-dependent pseudopotential for Na$_2^+$. The supplementary material (SM) plots two of the exactly calculated parameters and their corresponding coordinate-dependent fits (Fig. S1), and presents a table (Table S1) that summarizes all of the fitting parameters and rational polynomial functions used for the complete expression of our coordinate-dependent pseudopotential for Na$_2^+$.5

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FIG. 1. Cross-sections of (a) $U^\text{Na}_2^+ (r_1, r_2; R)$, (b) $U^\text{Na}_2^+ (r_1) + U^\text{Na}_2^+ (r_2)$, and (c) $\xi(r_1, r_2; R)$ taken through the bonding axis at an internuclear distance of 3.7 Å. The white dots show the location of the Na+ nuclei.

With the same simulation details described in our original paper, we then used the corrected expression for sodium dimer cation’s coordinate-dependent potential to calculate the ground-state potential energy curve (PEC) for Na2+ as a function of the internuclear separation. We note that we switched the reported vibrational frequencies in our original manuscript: the higher frequency, 113 cm\(^{-1}\), should be attributed to the coordinate obtained with our coordinate-dependent pseudopotential and the lower, 104 cm\(^{-1}\), to that of the FCA. The frequency obtained via a calculation with our coordinate-dependent pseudopotential for Na2+ yields a value close to the HF-calculated frequency of 117 cm\(^{-1}\) obtained with our basis set. Figure 3 compares our PEC to that obtained employing “frozen core” potentials and those using single-point, all-electron HF calculations for the LUMO of Na2+ and the HOMO of Na2+, plotted as the energy of those orbitals plus the classical nuclear repulsion. Performing a geometry optimization on Na2+ at the HF level of theory yields an equilibrium bond length of 3.68 Å, which is very close to the value of 3.69 Å obtained with our coordinate-dependent pseudopotential and significantly lower than the value of 3.98 Å calculated using a superposition of our unoptimized FCA potentials. As is evident, there is no change in the equilibrium bond distance, nor in the vibrational frequency and well depth from that presented in our original paper. This is because our method is built on the PK formalism, which guarantees the precise determination of the energy for the molecule’s valence electron. Thus, although the mathematical error led to an incorrect description for the charge density of Na2+’s bonding electron, there was no effect on the calculated energies.

Finally, we note that the two distinct lobes of charge density that we presented previously for this molecule were also affected by our basis set coding error; the correct charge density is more spherical and exhibits relatively little difference from that generated using the sum of FCA atomic pseudopotentials (see Fig. S2 in the SM\(^2\)).

Overall, none of the discussion in our original manuscript about designing potentials to correct for the lack of norm-conservation and core-core polarization inherent in the FCA, including all of the discussion of the effects that correcting for the FCA has on the Na2+ molecule, is affected by our error. Our error did affect the details of how our new formalism is applied to Na2+, including overestimating the magnitude of the failure of the FCA, but the formalism itself, which we will apply in future work, is entirely unaffected, and the correct application to Na2+ is presented here.

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5. See supplementary material at http://dx.doi.org/10.1063/1.4823770 for various plots and a table that gives precise information regarding the expression used for fitting the corrective function.