

Erratum: “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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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 for the Na_2^+ . Although our error affected the application of our method to Na_2^+ , as described further below, it did not affect the calculations related to the “frozen core” potential for this molecule, nor did it affect the method itself or any of the discussion in our original manuscript related to the presentation of the method. Thus, our method is correct and should still be widely applicable, but the particular presentation for Na_2^+ in our original manuscript is incorrect.

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 $U_{\text{eff}}^{\text{Na}_2^+}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$, $U_{\text{eff}}^{\text{Na}^+}(\mathbf{r}_1) + U_{\text{eff}}^{\text{Na}^+}(\mathbf{r}_2)$, and $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ (as defined in Eqs. (8)–(10) of our original manuscript¹), where the cross-sections shown are taken through the internuclear bonding axis at $\mathbf{R} = 3.7 \text{ \AA}$, 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 $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ functions at a number of internuclear distances to an analytic function.¹ The new functional form we chose was

$$\begin{aligned} \xi_{\text{fit}}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R}) = & b[e^{-c\mathbf{r}_1^2} + e^{-c\mathbf{r}_2^2}] + f[\mathbf{r}_1^2 e^{-g\mathbf{r}_1^2} + \mathbf{r}_2^2 e^{-g\mathbf{r}_2^2}] \\ & + h[e^{-k\mathbf{r}_{1\text{cm}}^2} + e^{-k\mathbf{r}_{2\text{cm}}^2}] \\ & + l[\mathbf{r}_{1\text{cm}}^2 e^{-m\mathbf{r}_{1\text{cm}}^2} + \mathbf{r}_{2\text{cm}}^2 e^{-m\mathbf{r}_{2\text{cm}}^2}] + i e^{-j^2 \mathbf{r}_{\text{com}}^4}, \end{aligned} \quad (1)$$

which consists of identical atom-centered Gaussian and $\mathbf{r}^2 e^{-\mathbf{r}^2}$ functions, one $e^{-\mathbf{r}^4}$ function at the molecule’s COM, and identical Gaussian and $\mathbf{r}^2 e^{-\mathbf{r}^2}$ 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, $b(\mathbf{R}) - j(\mathbf{R})$, and Figure 2 shows a fit of $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ with the above function at a representative internuclear 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 \mathbf{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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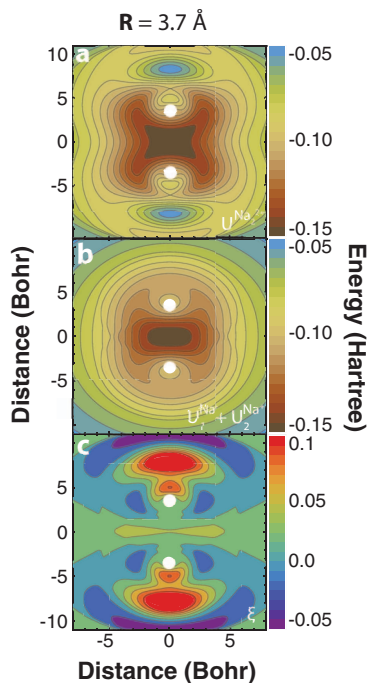


FIG. 1. Cross-sections of (a) $U_{\text{eff}}^{\text{Na}_2^+}(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$, (b) $U_{\text{eff}}^{\text{Na}^+}(\mathbf{r}_1) + U_{\text{eff}}^{\text{Na}^+}(\mathbf{r}_2)$, and (c) $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ taken through the bonding axis at an internuclear 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,¹ we then used the corrected expression for sodium dimer cation's coordinate-dependent potential to calculate the ground-state potential energy curve (PEC) for Na_2^+ 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 calculation performed 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 Na_2^+ 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 Na_2^{2+} and the HOMO of Na_2^+ , plotted as the energy of those orbitals plus the classical nuclear repulsion. Performing a geometry optimization on Na_2^+ 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

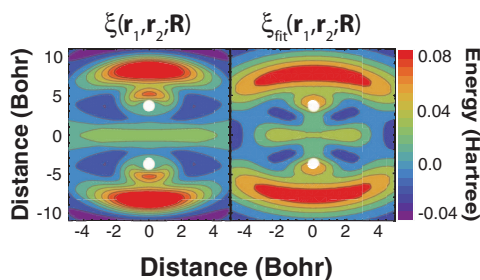


FIG. 2. Slice of the numerically calculated $\xi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{R})$ for Na_2^+ (left) and fit of this slice (right) to Eq. (1). Slices were taken through the bonding axis with an internuclear spacing of 4.0 Å, and all axis labels are in atomic units. The white dots show the location of the Na^+ nuclei.

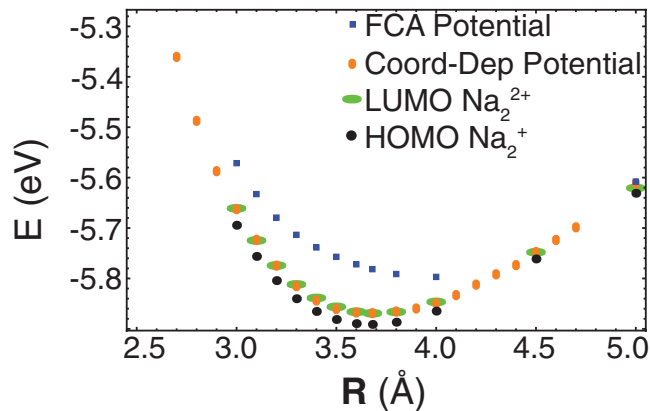


FIG. 3. Gas-phase potential energy surfaces of the Na_2^+ system calculated from mixed quantum/classical MD simulations with a frozen core pseudopotential (blue squares), our coordinate-dependent pseudopotential (orange rounded rectangles), and from fixed-point restricted HF calculations of the LUMO of Na_2^{2+} (green ellipses) and unrestricted HF calculations of the HOMO of Na_2^+ (black circles) using *Gaussian 03*.

pseudopotential and significantly lower than the value of 3.98 Å calculated using a superposition of our unoptimized FCA potentials.⁴ 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.¹ 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 Na_2^+ '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 molecule¹ 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 SM⁵).

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 Na_2^+ molecule, is affected by our error. Our error did affect the details of how our new formalism is applied to Na_2^+ , 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 Na_2^+ is presented here.

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⁵See 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.