New generation of effective core potentials from correlated calculations: 2nd row elements

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(I. INTRODUCTION)

The effective core potential (ECP) approximation has been vital in electronic structure calculations for several decades. An ECP is used to replace an atom’s core (nucleus and tightly bound electrons) and is constructed to mimic the original core’s effects on the valence electrons. This approximation provides important benefits such as the removal of large energy scales associated with the core electrons while simultaneously enabling the implicit incorporation of the core’s relativistic effects. It generates smoother charge densities around the nucleus which, for instance, allows the use of much smaller plane wave basis cutoff energies or less extensive gaussian basis sets. Consequently, in many cases, the availability of accurate ECPs can be the deciding factor for whether a calculation is even feasible or not. Given that the scope and accuracy of many-body electronic structure methods are continually increasing (true for both stochastic and basis set approaches, see \cite{14}), it is important that the errors of the ECP approximation be kept as small as possible or at least kept comparable to other systematic errors that may be present.

Historically, ECPs have often been generated within effective mean-field (single-particle) theories where the concept of core-valence partitioning follows rather naturally. A number of approaches have been established in the Density Functional Theory (DFT) \cite{6,12}, see also review \cite{13}. For the review of Dirac-Fock energy consistent constructions see \cite{14}. Although generating valence-only Hamiltonians is more straightforward in an effective one-particle setting, the performance of such ECPs within many-body theories is not guaranteed and can lead to results of mixed quality \cite{15} which can require adjustments to make them reliable within these theories \cite{16,17}. In order to achieve more consistent and systematic accuracy within many-body theories, we have recently proposed a general framework and provided examples of a new generation of correlation consistent ECPs (ccECPs) \cite{15} that aim to reach beyond the current status. The key principles included the use of many-body constructions and benchmarking to ascertain the quality of the ECPs from the outset. The first component of our strategy was based on near-isospectrality, within a subspace of valence states, between the all-electron and ECP Hamiltonians. Furthermore, the ECP properties were studied not only for atoms but also for small molecules to probe for transferability in bonded situations in order to validate their overall quality.

Remarkably, for the first row, we found that it was possible to derive ECPs that show significant improvements in various valence properties at the CCSD(T) level of theory when compared with existing ECP tables or the all-electron uncorrelated-core (UC) approximation where correlations from the core are suppressed. Quite surprisingly this was achieved with simple, “minimal”, non-divergent ECP parameterizations, i.e., with very few gaussians per nonlocal channel.

In order to maintain the simplicity and direct connec-
tion of the ECP to the original Hamiltonian, the solution was formulated as an inverse problem. Namely, we searched for an effective Hamiltonian operator that reproduces a given set of many-body eigenenergies and eigenstates, outside the core region, as closely as possible. Not surprisingly, this can lead to an ill-conditioned problem (high sensitivity to inputs) and/or a complicated optimization landscape with many near-degenerate minima. Consequently, such optimizations can be rather difficult. Such difficulties can be understood conceptually, for instance, if one considers the well-known example from the spectral theory that two operators with different domains can have the same spectrum, i.e., they can be exactly isospectral. This non-uniqueness suggests that the problem requires adequate and proper constraining in order to arrive at a desirable solution with a reasonable amount of effort. For the B, C, N, O and S elements, we were able to accomplish just that and produced ECPs for these atoms that exceed the accuracy of existing tabulated ECPs and that have led to significant improvements in transferability including extreme non-equilibrium conformations such as the molecular dissociation limits at the short bond lengths. Note that this limit is particularly challenging since it directly probes whether the ECP correctly mimics the (missing) core charge at short lengths.

We also aimed to construct ECPs that are simple and can be employed in a variety of electronic structure packages and methods, i.e., as widely applicable as possible. To this end, we chose a non-singular form, for ease of use in quantum Monte Carlo calculations as well as in plane wave codes, parameterized by a short sum of gaussians, similarly to our previous work.

Another aspect of our recently constructed ECPs was to probe for the transferability in bonds both near and out of the equilibrium configurations, having in mind, for example, high-pressure applications in future. Therefore we monitored discrepancies of dimer binding curves including short bond lengths up to the dissociation limit, where the binding energy goes to zero for the compressed bond. In cases where larger errors are present, we included the dimer into the construction as an additional constraint that improved the quality of the resulting ECPs. Indeed, we found that the key molecular properties were more accurately reproduced. As the independent probe of transferability, we then used hydride and oxide molecules. Further benchmarks and testing will come from future applications for systems where all-electron correlated calculations can be carried out.

The constructed ECPs that we present below are not meant to be definitive. It is clear that with more elaborate forms, say, with a larger number of free parameters, the accuracy can be still improved. Another aspect is that different applications might require further refinement or even new constructions. For example, alkaline elements have nominally large cores and one or two valence electrons. Clearly, there are applications where this would not provide an accurate replacement of the all-electron Hamiltonian (high pressures) and the inclusion of the outermost shell from the core to the valence space might be needed. This implies that one needs more options to guarantee the accuracy in various physical or chemical applications. Therefore keeping track of updates and any new constructions, as well as maintaining benchmark sets is an important part of providing clear choices and validations for future use of ECPs.

The paper is organized as follows. The next sections outline the conceptual and construction details. The result section presents our ECPs together with several existing ones for comparison. The significant errors that appear to be inherent for Ne-cores in particular settings (short polar bonds) motivated us to construct also He-core ECPs that significantly improve the accuracy of ECPs with Ne-core partitioning and serve also as benchmarks for comparisons. In conclusions, we further discuss the obtained results and their implications.

II. ECP ATOMIC CORRELATION ENERGIES

As we proceeded with electronic structure calculations we found very useful to look in a more quantitative manner at the energy contributions from core-core, core-valence, and valence-valence correlations as well as to their Hartree-Fock/Dirac-Fock counterparts. This provided additional insights into how various components of the energy get modified and respond to ECP changes that ultimately enabled us to improve the optimization and helped the final high accuracy tuning. In order to understand this point better, we have analyzed the errors from the Hartree-Fock (HF) and correlation contributions to the CCSD(T) spectral energies for an illustrative cases of atoms (with further details on CCSD(T) calculations given throughout the paper as well as in SI materials). Relativity in all-electron calculations was included through the 10th-order Douglas-Kroll-Hess Hamiltonian for both HF and CCSD(T) approaches.

In Figs. 1 and 2 we show examples of the spread of HF and CCSD(T) valence-valence correlation errors across a number of previously tabulated ECPs, which employ a wide variety of parameterizations, for the cases of the silicon and phosphorus atoms. There, we plot the spread of the following quantities over a variety of ECPs:

$$\Delta HF_s = \Delta E_s^{PP} - \Delta E_s^{AE}$$

where \(\Delta E_s\) represents the energy gap between a given state and the ground state,

$$\Delta cVV_s = |VV_{corr,s}^{PP}| - |VV_{corr,s}^{AE}|$$

where \(VV_{corr}\) is the valence-valence correlation energy. In these figures, the spread (represented by the shaded areas) are bounded by the maximum discrepancy (upper bound) and minimum discrepancy (lower bound) among the various ECPs. For the ECP cases, the valence-valence correlation is taken to be the fully correlated
CCSD(T) energy of a particular state. For the all-electron case, the valence-valence correlation is taken to be the UC CCSD(T) energy of a particular state.

FIG. 1: For the silicon atom, the spread of CCSD(T) valence-valence correlation errors ($\Delta c_{VV}$) and spread of HF errors ($\Delta HF$) for various excitation energies from a variety of previously tabulated ECPs, in particular, BFD[19], CRENBL[20], SBKJC[21], STU[22] and TN-DF[23].

There are several observations that can be gleaned from these plots. The first is that the ECPs' correlation energies are on average larger than the corresponding all-electron valence-only correlated values with the increase varying between 0 and 0.15 eV. This has been known for some time, see the analysis by Dolg[24]. The reason is the absence of the radial node(s) and increased smoothness of ECP (pseudo)orbitals since this increases the probability for unlike spin pairs of electrons to encounter each other, thus increasing the correlation energy. However, the next striking feature is the rigidity of the correlated energy differences across various ECPs, regardless of construction, whether it shows singular or bounded/smooth behavior of local and nonlocal terms at the origin or other details. Essentially the ECP correlation energies are almost invariant to the the form or the construction of ECP, typically within 0.02 eV or less. Consequently, the largest differences between ECPs for atomic spectra come from fluctuations that originate in the HF component of energy differences. Finally, the third point is that aiming for atomic spectra accuracy better than 0.1 eV requires the HF component to “compensate” for the rigid correlation contribution component for a number of states. The interplay of correlation and mean-field energy components becomes even more intricate in molecular bonds as we will see later.

III. CONSTRUCTION

The strategy that we employ to generate our ECPs is a combination of many-body energy consistency and single-body norm conservation. We provide the details of each and how they are combined to form our full objective function in this section.

A. Many-body Energy Consistency

In order to account for correlation when generating our ECPs, we have employed a spin-unrestricted CCSD(T) energy consistency scheme as part of our full objective function.

The details of this scheme are as follows: For a given atom, we first generate a large number of all-electron reference atomic states which includes various ionizations and spin-multiplicities. The states are calculated with the fully correlated (both core and valence electrons) spin-unrestricted CCSD(T) method. We account for relativity by using the 10th order Douglas-Kroll-Hess Hamiltonian[25]. We formulate this part of the objective function by calculating the same atomic states with a parameterized ECP at the same level of theory, and then vary the parameters until the gaps between these states and the neutral ground state agree with that from the all-electron to a satisfying level. The discrepancies of the ECP gaps relative to the all-electron gaps are minimized in the least squares way which defines the first component of our objective function, $\mathcal{E}^2$, given by

$$\mathcal{E}^2 = \sum_s (\Delta E^s_{PP} - \Delta E^s_{AE})^2,$$

where $s$ labels a given atomic state and $\Delta E_s$ is the energy gap between the state and the neutral ground state and
“PP” and “AE” label the ECP and all-electron gaps, respectively.

The energetics from all-electron and ECP were calculated with the MOLPRO quantum chemistry package \cite{20}. For all atoms, the uncontracted aug-cc-pCV5Z basis set \cite{27}, where core state correlation functions are present, was utilized. This same basis was used for calculating both the all-electron and ECP gaps in order to construct similar basis set errors between the two which would largely cancel when calculating their difference in Eq. \ref{eq:5}. Quantitative estimates of the residual finite basis set errors were given in our previous work \cite{18} for a test set of atoms from the 1st and 2nd row.

We chose not to use the $E^2$ objective function exclusively when training our ECPs given that in doing so we observed an overall large increase in error of the HF gaps and subsequently poorer transferability when calculating potential energy surfaces of diatomic molecules (dimers and oxides) at the CCSD(T) level of theory. We suspect this is due to the rigidity in the ECP correlation energies as outlined in section \ref{sec:B}, namely, in order to reduce the total error of the CCSD(T) gap, the magnitude of the HF error increases to compensate the error from the more rigid correlations. We observed that reaching small gap errors at the many-body level at the full expense of the HF gap errors showed tendencies to increase transferability errors. In fact, the best results came from a balance between the errors in correlation and HF components. In addition, significant variational freedom inside the core is proved to be helpful and we have therefore included a single-body norm conservation into our objective function, as outlined in the next subsection, in order to strike this balance.

\section*{B. Single-body Norm Conservation}

In order to maintain accuracy at the HF level of theory, we employed a norm conservation scheme as another component of our full objective function. We have taken a strategy similar to what has been used in previous works \cite{21, 23, 28, 29}, however, the specifics of our approach are as follows: We first construct an “exact” radial pseudo-orbital (referred to simply as “pseudo-orbital” in what follows) of angular momentum $l$, $\phi_l$, which we define as

$$
\phi_l(r) = \begin{cases} 
  r^l f_l(r) & , r \leq R_c \\
  \phi_l^{(AE)} & , r > R_c 
\end{cases}
$$

where $f_l$ is a 6-term polynomial chosen to be nodeless and non-zero at the origin given that our ECPs are non-singular (as outlined in the next section) and $R_c$ is a chosen core radius beyond which the pseudo-orbital is given by the all-electron orbital, $\phi_l^{(AE)}$, obtained from solving the all-electron scalar relativistic HF equations. The coefficients of $f_l$ are obtained by requiring that the pseudo-orbital’s value and first four derivatives match those of the all-electron orbital at $r = R_c$ as well as requiring that the two norms agree for $0 \leq r \leq R_c$. In so doing, we obtain a pseudo-orbital whose logarithmic derivative at $r = R_c$ agrees with that of the all-electron orbital \cite{6}.

Once the pseudo-orbital is constructed, rather than using an inversion procedure to generate the ionic potential, we follow a similar approach as outlined for the many-body energy consistency component whereby we vary our parameterized ECP form to minimize the discrepancy between its orbitals and the pseudo-orbitals in the least squares way. This constitutes the second component, $N^2$, of our full objective function which is given by

$$
N^2 = \sum_l \int_0^\infty dr \, r^2 (\phi_l^{PP} - \phi_l)^2,
$$

where $\{\phi_l^{PP}\}$ is the set of orbitals obtained from solving the valence-only HF equations with the parameterized ECP.

In the cases of S and P, we slightly modified the above approach and allowed more freedom inside the core region by minimizing (with the least squares approach) the discrepancies from the all-electron orbital norms, values and first derivatives of the orbitals at the cutoff radius and the eigenvalues of the orbitals – allowing for any core shape necessary to reproduce these quantities.

\section*{C. Weighted Combination and Core-Valence Partitioning}

To form our full objective function, $O^2$, we take $E^2$ and $N^2$ as a linear combination,

$$
O^2 = E^2 + \alpha N^2,
$$

where $\alpha$ is an empirically chosen weight. To construct our ECP, we vary its parameters until $O^2$ is minimized. The value of $\alpha$ is chosen so as to strike a balance between the accuracy of the many-body and single-body properties of the ECP – or viewed in another way, we are allowing a violation of single-body norm conservation in order to achieve higher accuracies on the many-body spectral properties.

When using the conventional Ne-core and 3s3p valence, the transferability of the ECPs in particular environments was observed to be less than satisfying. This is particularly true for compressed polar bonds (as will be shown). In order to reach high many-body and single-body accuracies in these regimes as well, we have also generated He-core ECPs for all of the second row atoms. For these ECPs, we found that using $\alpha = 0$ did not introduce a significant negative impact to the single-body properties nor transferability and therefore we used this value of $\alpha$ for our objective function when generating our He-core ECPs.

We have applied the construction outlined in this section to all the second row atoms, Na-Ar. For all optimizations, we have used the DONLP2 solver of Spellucci.
to generate the optimal parameter sets for all ECPs. The methodologies used in DONLP2 are outlined in [31] and [32].

IV. ECP FORM

The ECPs we have constructed have the following form

\[ V_{i}^{pp} = V_{loc}(r_{i}) + \sum_{l=0}^{l_{\text{max}}} \sum_{m} V_{i}(r_{i}) |lm\rangle \langle lm|, \tag{7} \]

where \( r_{i} \) is the radial distance of electron \( i \) from the core’s origin and \( l_{\text{max}} \) is chosen to be the maximum occupied angular momentum channel from the ground state core.

The local potential, \( V_{loc} \), is taken to be

\[ V_{loc}(r) = -\frac{Z_{\text{eff}}}{r} (1 - e^{-\alpha r^2}) + \alpha Z_{\text{eff}} r e^{-\beta r^2} + \gamma e^{-\delta r^2}, \tag{8} \]

where \( Z_{\text{eff}} = Z - Z_{\text{cor}} \) is the pseudo-atom’s total core charge. The set of non-local potentials, \( \{V_{i}\} \), are parameterized by a short sum of gaussians

\[ V_{i}(r) = \sum_{l} \beta_{l} e^{-\alpha_{l} r^2}. \tag{9} \]

The Greek letter parameters are all varied in the minimization of our objective function. This simple form keeps the volume of the parameter space as small as practically possible and therefore helps to simplify the optimization problem.

V. RESULTS

For all 2nd row atoms, we share in Tables I, II, III, IV, V, VI, VII, and VIII the all-electron CCSD(T) valence ionization potentials and (if bound) the electron affinity along with the discrepancies of the same quantities from various core approximations which includes all-electron uncorrelated core (UC), a number of previously tabulated ECPs [19, 21–23] and our Ne-core and He-core correlation consistent ECPs, ccECP[He] and ccECP[Ne], respectively. We also share the discrepancies from all-electron UCCSD(T) potential energy surfaces for one or two diatomic molecules for all the atoms in Figs. 3, 4, 5, 6, 7, 8, 9 and 10. For the cases of oxides, we utilized our previously published oxygen ECP [18] when calculating potential energy surfaces for our ECPs and for all other ECPs we used that table’s corresponding oxygen ECP. For the molecular discrepancies, we span a large range of geometries in all cases, from near the dissociation threshold (\( \approx 0.05 \) Å) on the left to just past equilibrium. For argon, we used a well-tuned unpublished hydrogen ECP for all cases other than uncorrelated core. Our ECP parameter sets are shared in Tables XI and XII.

In the following subsections, we provide a discussion for each pseudoatom’s atomic and molecular accuracies, in turn, and summarize the results.

A. Sodium

In the case of sodium, the atomic and molecular results of our Ne-core and He-core ECPs are shared in Table I and Fig. 3 respectively. For the case of the Ne-core, our construction led to a significant improvement of the atom’s first ionization potential, when compared to the all-electron UCCSD(T) result, relative to the previously tabulated ECPs as well as the uncorrelated core (UC) result – the error being roughly a factor of 3 smaller than the other ECPs and roughly a factor of 2 smaller than UC. The electron affinity of our Ne-core ECP is also in good agreement with the all-electron result with an error that is less than 0.01 eV. In the case of our He-core ECP, the agreement with the all-electron atom is better still and for each quantity, the errors are at sub meV scales.

For the Na2 and NaO molecules, the accuracies of both of our core partitions are also quite high with our Ne-core and He-core ECPs being within 0.05 eV and 0.01 eV of the all-electron UCCSD(T) result over the full range of geometries, respectively.

B. Magnesium

For magnesium, the atomic and molecular results of our Ne-core and He-core ECPs are shared in Table II and Fig. 4 respectively. The Ne-core partition shows an increased accuracy over UC and the previously tabulated ECPs with respect to the first and second ionization potentials. The He-core partition further increases the accuracy by more than an order of magnitude, with errors less than a meV for these quantities.

In the case of the MgO molecule, our Ne-core ECP shows better agreement with all-electron UCCSD(T) at shorter atomic separations than both UC and previously tabulated ECPs and at equilibrium, the agreement is within chemical accuracy. Our He-core ECP improves upon this further, with errors less than 0.01 eV across all geometries plotted.

C. Aluminum

For aluminum, the atomic and molecular results of our Ne-core and He-core ECPs are shared in Table III and Fig. 5 respectively. In the Ne-core case, the errors over the ionization potentials and the electron affinity were not improved over the other core approximations but instead remained comparable. We note the lower variational freedom for our case due to bounded forms and smaller radial range when compared with some of the
constructions. However, in the case of the He-core, we observed errors less than a hundredth of an eV.

The Al₂ molecule is described well by both core partitions, both being within chemical accuracy scales. For the AlO molecule, similar to previously tabulated ECPs, our Ne-core ECP is overbound by tenths of eV as the molecule is compressed towards dissociation. This potentially signifies a limitation of this particular choice of core for this type of environment, namely, compressed polar bonds. We suspect that key contributors to the error in this regime are a breakdown of the assumed point-charge interactions of the cores and also the neglect core-valence overlaps \cite{14, 35}. For our smaller He-core ECP, we see that these difficulties evaporate and we observe errors well within chemical accuracy.

D. Silicon

For silicon, the atomic and molecular results of our Ne-core and He-core ECPs are shared in Table \textbf{V} and Fig. \textbf{6} respectively. In the Ne-core case, like Al, the accuracies among the ionization potentials and electron affinity were not improved over the other core approximations, though the He-core ECP shows errors smaller than chemical accuracy for all of these quantities. The results from the Ne-core ECP potentially reveal the limitations of this particular core partition.

In the case of the silicon dimer, both core partitions perform very well and their errors at the UCCSD(T) level are no more than about 0.02 eV. The SiO molecule shows similar and profound discrepancies for the Ne-core ECP as was seen in AlO. At short atomic separations, the pseudo-molecule is severely overbound for all tested ECPs including our Ne-core partition. Interestingly, at equilibrium, the agreement for our ECP and some others is much better and is within chemical accuracy. For our He-core ECP, the errors are significantly reduced and we observe chemical accuracy agreement across all geometries plotted. On this element, it is clearly visible that atomic spectrum is not sufficient to assess the overall quality of the ECPs. Seemingly, BFD, TN, and STU have somewhat smaller energy discrepancies than our Ne-core ECP. However, molecular calculations reveal lower or even significantly lower transferability. In fact, our Ne-core ECP is on par with SBKJC that however is unbounded \((1/r^2)\) terms so that our variational freedom is then significantly lower in comparison.

E. Phosphorus

For phosphorous, the atomic and molecular results of our Ne-core and He-core ECPs are shared in Table \textbf{V} and Fig. \textbf{7} respectively. For the case of our Ne-core partition, we observed that comparable accuracies of the atomic properties were only achievable with respect to the other core approximations. However, significant improvement was again achieved for the case of our He-core partition.

For the case of P₂, both core partitions perform well with the Ne-core ECP obtaining maximum errors that are only marginally larger than chemical accuracy and the He-core ECP's errors being a factor of 2-3 smaller still. The results from PO are also quite good for both partitions. At equilibrium, both He- and Ne-core ECPs show errors no more than about 0.01 eV. For our He-core ECP, this level of accuracy is maintained as the bond is compressed, however, the Ne-core ECP at these shorter separations begins to overbind. Note that our constructions compete in overall optimality with SBKJC while having smaller variational freedom in bounded potentials. In addition, the molecular results show rather nonsystematic behavior for STU ECPs that are different (underbinding) from the rest of the row (typically, overbinding).

F. Sulfur

For sulfur, the atomic and molecular results of our Ne-core and He-core ECPs are shared in Table \textbf{VI} and Fig. \textbf{8} respectively. In this case, the accuracies of the Ne-core ECP at the UCCSD(T) level are rather good with errors within chemical accuracies throughout all bond lengths plotted for both S₂ and SO molecules. And for our He-core ECP, we again see the benefit of this particular choice of core-valence partitioning where the atomic accuracies show large improvements over the other Ne-core approximations and \(\approx 0.01 - 0.02\) eV accuracy is achieved for both the sulfur dimer and oxide across all geometries plotted.

G. Chlorine

For chlorine, the atomic and molecular results of our Ne-core and He-core ECPs are shared in table \textbf{VII} and figure \textbf{9} respectively. For this case, we only observed a significant improvement of the ionization potentials and electron affinity for our He-core ECP – its errors reaching no more than about 0.1 eV even for very deeply ionized cases.

Our construction, however, led to He- and Ne-core ECPs that reproduce the all-electron Cl₂ and ClO potential energy surfaces quite well – where the larger core achieves errors no more than about chemical accuracy across all geometries in both molecules and the smaller core remaining well within chemical accuracy for these same quantities.

H. Argon

For argon, the atomic and molecular results of our Ne-core and He-core ECPs are shared in Table \textbf{VIII} and Fig.
respectively. With respect to the atomic properties, the Ne-core ECP performs well in this case with a total mean absolute deviation that is comparable to the all-electron uncorrelated core results. The He-core again performs even better where the total mean absolute deviation is improved over our Ne-core ECP by another 0.1 eV. To test the ECPs’ performances in a molecular setting we calculated the errors from the all-electron UCCSD(T) ArH+ binding curve. Both core partitions show high accuracies for this case where the Ne-core and He-core errors are no larger than \( \approx 0.06 \) eV and \( \approx 0.01 \) eV in magnitude, respectively.

I. Molecular parameters and total energies

We compiled all the results for molecular equilibrium parameters into the Tab. IX. The statistics provide useful information for an overall performance of the presented constructions as well as comparison with previously published tables. We have achieved rather significant improvements in the molecular properties due to the more flat discrepancy curves than other ECPs. In general, the ECPs have a tendency to overbind for short bonds and the cause is the missing core charge and the related core-valence repulsion. Interestingly enough, except for Al and Si, we were able to keep these biases typically below 0.05 eV with mildly increased deviations (0.1 eV) at very small bond length for Mg and Ar. Clearly, minor further improvements might be still possible although we expect that one would encounter diminishing returns unless the ECP form is further generalized. On the other hand, He-core framework clearly eliminates these deficiencies and provide very high accuracy across the whole row. Finally, we list total HF and correlation energies from UCCSD(T) as extrapolated to the complete basis set limit. While HF energies are saturated to about 0.1 mHa or better in all cases, for Ne-core we estimate extrapolation errors on correlation energies to be within about 1 mHa. For He-core correlation energies we guess underestimation by about 3 mHa for Na and up to about 6 mHa for Ar, showing limitations of 5Z basis set and excitations up to perturbational triples to fully capture the many-body effects of 16 electrons. This estimate comes from an approximate analysis of core-core, core-valence and valence-valence correlation energy components in all-electron calculations \[26] with an added correction from Dolg [24] that reflects increase in correlations in the ECP setting. Finally, the subsequent tables provide the ccECP parameters that are available also at the website http://pseudopotentiallibrary.org together with basis sets up to 5Z level. Additional data can be found also in Supplementary Information.
TABLE I: All-electron (AE) UCCSD(T) electron affinity and ionization potential of Na along with the errors from uncorrelated core (UC), ECPs and for information purposes also from experiment (Exp.). The uncontracted aug-cc-pCV5Z basis was used for all calculations. MAD is the mean absolute deviation of excitation energies, while MARE is the mean absolute relative error. All values in eV.

| Qty. | Exp. | AE    | Discrepancies from AE |
|------|------|-------|-----------------------|
|      |      |       | UC | SBKJC | BFD | TN-DF | STU | ccECP[Ne] | ccECP[He] |
| IP(I) | 5.1391$^a$ | 5.1334 | -0.0613 | -0.1359 | -0.1173 | -0.1691 | -0.1779 | -0.0603 | -0.0053 |
| EA   | 0.5479$^b$ | 0.5470 | -0.0017 | 0.0005 | 0.0030 | 0.0025 | 0.0026 | 0.0077 | 0.0003 |
| MAD  | 0.0616 | 0.0926 | 0.0608 | 0.0882 | 0.0900 | 0.0371 | 0.0006 |
| MARE | 0.0134 | 0.0184 | 0.0200 | 0.0192 | 0.0197 | 0.0135 | 0.0004 |

$^a$ Reference [33]

$^b$ Reference [34]

FIG. 3: Binding energy discrepancies for (a) Na$_2$ and (b) NaO molecules. The binding curves are relative to the AE UCCSD(T) binding curve. The shaded region indicates a discrepancy of chemical accuracy in either direction.

TABLE II: All-electron UCCSD(T) ionization potentials for Mg along with the errors from uncorrelated core (UC) and ECPs. The uncontracted aug-cc-pCV5Z basis was used for all calculations. All values in eV. See Tab. I for further description.

| Qty. | Exp. | AE    | Discrepancies from AE |
|------|------|-------|-----------------------|
|      |      |       | UC | SBKJC | BFD | TN-DF | STU | ccECP[Ne] | ccECP[He] |
| IP(I) | 7.6462$^a$ | 7.6400 | -0.0062 | -0.0081 | -0.0072 | -0.0093 | -0.0061 | -0.0578 | -0.0006 |
| IP(II) | 15.0354$^a$ | 15.0287 | -0.0077 | -0.0088 | -0.0093 | -0.0093 | -0.0092 | -0.0077 | -0.0001 |
| MAD  | 0.1919 | 0.1944 | 0.1812 | 0.1791 | 0.1687 | 0.1314 | 0.0003 |
| MARE | 0.0159 | 0.0158 | 0.0144 | 0.0135 | 0.0132 | 0.0106 | 0.0000 |

$^a$ Reference [33]
FIG. 4: Binding energy discrepancies for the MgO molecule. The binding curves are relative to the AE UCCSD(T) binding curve. The shaded region indicates a discrepancy of chemical accuracy in either direction.

TABLE III: All-electron (AE) UCCSD(T) ionization potentials and electron affinity of Al along with the errors from the uncorrelated core (UC) and ECPs. Exp. gives experimental values for information purposes. The uncontracted aug-cc-pCV5Z basis was used for all calculations. AMAD is the mean absolute deviation for all excitation energies, LMAD is the mean absolute deviation for the first and second ionization potentials and electron affinity, while MARE is the mean absolute relative error for all states. All values in eV.

| Qty. | Exp. | AE | Discrepancies from AE |
|------|------|----|-----------------------|
|      |      |    | UC SBKJC BFD TN-DF STU ccECP[Ne] ccECP[He] |
| IP(I) | 5.9858 \(^a\) | 5.9606 | 0.0045 0.0214 0.0135 0.0167 0.0667 0.0236 0.0024 |
| IP(II) | 18.8296 \(^a\) | 18.8216 | -0.6988 -0.1720 -0.1588 -0.1408 -0.0862 -0.1895 -0.0061 |
| IP(III) | 28.4765 \(^a\) | 28.4474 | -0.3588 -0.4331 -0.3339 -0.3640 -0.3384 -0.4119 -0.0064 |
| EA | 0.4328 \(^b\) | 0.4183 | -0.0165 0.0215 0.0225 0.0182 0.0294 0.0235 0.0009 |
| AMAD | 0.1374 | 0.1820 0.1322 0.1349 0.1392 0.1631 0.0049 |
| LMAD | 0.0636 | 0.0716 0.0649 0.0586 0.0608 0.0802 0.0032 |
| MARE | 0.0155 | 0.0198 0.0191 0.0166 0.0245 0.0235 0.0009 |

\(^a\) Reference [33]  
\(^b\) Reference [34]

TABLE IV: All-electron (AE) UCCSD(T) ionization potentials and electron affinity of Si along with the errors from uncorrelated core (UC) and ECPs. The uncontracted aug-cc-pCV5Z basis was used for all calculations. All values in eV. See Tab. III for further description.

| Qty. | Exp. | AE | Discrepancies from AE |
|------|------|----|-----------------------|
|      |      |    | UC SBKJC BFD TN-DF STU ccECP[Ne] ccECP[He] |
| IP(I) | 8.1517 \(^a\) | 8.1392 | -0.0055 0.0190 0.0152 0.0183 0.0977 0.0165 -0.0055 |
| IP(II) | 16.3459 \(^a\) | 16.3014 | -0.0320 -0.0896 -0.0131 -0.0972 0.1280 -0.0251 -0.0210 |
| IP(III) | 33.4930 \(^a\) | 33.4791 | -0.2143 -0.2827 -0.1909 -0.2143 -0.0744 -0.2943 -0.0060 |
| IP(IV) | 45.1418 \(^a\) | 45.1325 | -0.5920 -0.3528 -0.4683 -0.1474 -0.6146 0.0412 |
| EA | 1.3895 \(^b\) | 1.3928 | 0.0097 0.0210 0.0144 0.0193 0.0417 -0.0238 -0.0004 |
| AMAD | 0.1326 | 0.1849 0.1173 0.1455 0.0978 0.1949 0.0148 |
| LMAD | 0.0157 | 0.0165 0.0142 0.0149 0.0891 0.0218 0.0090 |
| MARE | 0.0050 | 0.0079 0.0053 0.0067 0.0111 0.0086 0.0007 |

\(^a\) Reference [33]  
\(^b\) Reference [34]
FIG. 5: Binding energy discrepancies for (a) Al₂ and (b) AlO molecules. The binding curves are relative to the AE UCCSD(T) binding curve. The shaded region indicates a discrepancy of chemical accuracy in either direction.

TABLE V: All-electron (AE) UCCSD(T) ionization potentials and electron affinity of P along with the errors from uncorrelated core (UC) and ECPs. The uncontracted aug-cc-pCV5Z basis was used for all calculations. All values in eV. See Tab. III for further description.

| Qty   | Exp. | AE  | Discrepancies from AE |
|-------|------|-----|------------------------|
|       |      |     | UC  | SBKJC | BFD | TN-DF | STU | ccECP[Ne] | ccECP[He] |
| IP(I) | 10.4867 | 10.5104 | -0.0114 | 0.0171 | 0.0138 | 0.0221 | -0.0054 | 0.0292 | 0.0017 |
| IP(II)| 19.7695* | 19.7562 | -0.0355 | -0.0116 | -0.0003 | 0.0019 | 0.0050 | 0.0086 | -0.0165 |
| IP(III)| 30.2026* | 30.1328 | -0.0677 | -0.0798 | -0.0535 | -0.0522 | 0.0121 | -0.0536 | -0.0517 |
| IP(IV)| 51.4439* | 51.4304 | -0.2527 | -0.4559 | -0.2187 | -0.3254 | -0.2051 | -0.3353 | -0.0476 |
| IP(V) | 65.0251* | 65.0181 | -0.4402 | -0.9174 | -0.3825 | -0.6667 | -0.4504 | -0.3511 | -0.1314 |
| EA    | 0.7465* | 0.7003 | 0.0055 | -0.0103 | -0.0260 | -0.0102 | -0.0350 | 0.0123 | 0.0034 |
| AMAD  | 0.1355 | 0.2487 | 0.1158 | 0.1797 | 0.1188 | 0.1317 | 0.0421 |
| LMAD  | 0.0175 | 0.0130 | 0.0134 | 0.0114 | 0.0151 | 0.0167 | 0.0072 |
| MARE  | 0.0041 | 0.0071 | 0.0084 | 0.0058 | 0.0103 | 0.0056 | 0.0018 |

Reference [33]

Reference [34]
TABLE VI: All-electron (AE) UCCSD(T) valence ionization potentials and electron affinity of S along with the errors from uncorrelated core (UC) and ECPs. The uncontracted aug-cc-pCV5Z basis was used for all calculations. All values in eV. See Tab. III for further description.

| Qty  | Exp. | AE | ucECP[Ne] | ccECP[He] |
|------|------|----|-----------|-----------|
| IP(I) | 10.3600a | UC | SBKJC | BFD | TN-DF | STU | ccECP[Ne] | ccECP[He] |
| IP(II) | 23.3378a | 23.3950 | -0.0075 | 0.0231 | 0.0234 | 0.0098 | 0.2906 | 0.0225 | 0.0031 |
| IP(III) | 34.8600a | 34.8258 | -0.0670 | -0.0901 | 0.0010 | -0.0431 | 0.3369 | -0.0338 | -0.0183 |
| IP(IV) | 47.2220a | 47.2693 | -0.1042 | -0.1361 | -0.0673 | -0.1393 | 0.3210 | -0.1442 | -0.0566 |
| IP(V) | 72.5945a | 72.5882 | -0.2887 | -0.6879 | -0.2331 | -0.4965 | -0.0172 | -0.5411 | -0.0269 |
| IP(VI) | 88.0529a | 88.0550 | -0.4769 | -1.1502 | -0.3611 | -0.8586 | -0.4356 | -0.9851 | 0.0275 |
| EA | 2.0771b | 2.0500 | 0.0019 | 0.0020 | -0.0276 | 0.0004 | 0.0326 | 0.0015 | 0.0065 |

TABLE VII: All-electron (AE) UCCSD(T) ionization potentials and electron affinity of Cl along with the errors from uncorrelated core (UC) and ECPS. The uncontracted aug-cc-pCV5Z basis was used for all calculations. All values in eV. See Tab. III for further description.

| Qty  | Exp. | AE | ucECP[Ne] | ccECP[He] |
|------|------|----|-----------|-----------|
| IP(I) | 12.9676a | UC | SBKJC | BFD | TN-DF | STU | ccECP[Ne] | ccECP[He] |
| IP(II) | 23.8136a | 23.7399 | -0.0401 | -0.0649 | 0.0860 | -0.0743 | 0.2194 | -0.0839 | -0.0038 |
| IP(III) | 39.800a | 39.6860 | -0.0614 | 0.0099 | 0.0091 | -0.0126 | 0.4779 | 0.0233 | -0.0128 |
| IP(IV) | 53.242a | 53.1811 | -0.0939 | -0.0807 | -0.0816 | -0.0952 | 0.5020 | -0.0321 | -0.0477 |
| IP(V) | 67.680a | 67.6102 | -0.1328 | -0.2353 | -0.2471 | -0.2280 | 0.4487 | -0.1362 | -0.1023 |
| IP(VI) | 96.964a | 96.8961 | -0.3139 | -0.9935 | -0.8573 | -0.6785 | 0.0301 | -0.1292 | 0.0010 |
| IP(VII) | 114.2013a | 114.2079 | -0.5023 | -1.5507 | -0.2635 | -1.0900 | -0.4557 | -0.4249 | 0.0208 |
| EA | 3.6127b | 3.6210 | 0.0007 | 0.0193 | -0.0153 | 0.0079 | 0.0781 | -0.0184 | 0.0083 |

FIG. 7: Binding energy discrepancies for (a) P2 and (b) PO molecules. The binding curves are relative to the AE UCCSD(T) binding curve. The shaded region indicates a discrepancy of chemical accuracy in either direction.

(a) P2 binding curve discrepancies

(b) PO binding curve discrepancies
FIG. 8: Binding energy discrepancies for (a) S\textsubscript{2} and (b) SO molecules. The binding curves are relative to the AE UCCSD(T) binding curve. The shaded region indicates a discrepancy of chemical accuracy in either direction.

FIG. 9: Binding energy discrepancies for (a) Cl\textsubscript{2} and (b) ClO molecules. The binding curves are relative to the AE UCCSD(T) binding curve. The shaded region indicates a discrepancy of chemical accuracy in either direction.
TABLE VIII: All-electron (AE) UCCSD(T) ionization potentials for Ar along with the errors from uncorrelated core (UC) and ECPs. The uncontracted aug-cc-pCV5Z basis was used for all calculations. All values in eV. See Tab. III for further description.

| Qty. | Exp. | AE | Discrepancies from AE |
|------|------|----|-----------------------|
|      |      |    | UC | SBKJC | BFD | TN-DF | STU | ccECP[Ne] | ccECP[He] |
| IP(I) | 15.7596 | 15.7829 | -0.0172 | 0.0146 | -0.0156 | -0.0016 | -0.0116 | 0.0202 | 0.0376 |
| IP(II) | 27.6297 | 27.6005 | -0.0369 | -0.0386 | -0.0510 | -0.0567 | -0.0071 | -0.0126 | 0.0293 |
| IP(III) | 40.735 | 40.6121 | -0.0619 | -0.1305 | -0.1243 | -0.1451 | -0.0132 | -0.0862 | 0.0631 |
| IP(IV) | 59.58 | 59.2804 | -0.0835 | -0.0581 | -0.0243 | -0.0929 | 0.2038 | -0.0148 | 0.2038 |
| IP(V) | 74.84 | 74.7437 | -0.1178 | -0.2015 | -0.1742 | -0.2220 | 0.2387 | -0.0148 | 0.2038 |
| IP(VI) | 91.29 | 91.1085 | -0.1580 | -0.4181 | -0.4141 | -0.4046 | 0.2016 | -0.3698 | 0.2125 |
| IP(VII) | 124.41 | 124.3356 | -0.3353 | -1.3918 | 0.0652 | -0.9451 | -0.4787 | -0.1401 | 0.0419 |
| IP(VIII) | 143.4567 | 143.4706 | -0.5238 | -2.0213 | -0.0730 | -1.3990 | -0.9534 | -0.5716 | -0.0899 |
| AMAD | 0.1668 | 0.5343 | 0.1177 | 0.4084 | 0.2613 | 0.1691 | 0.0654 |
| LMAD | 0.0271 | 0.0266 | 0.0333 | 0.0291 | 0.0094 | 0.0164 | 0.0335 |
| MARE | 0.0019 | 0.0049 | 0.0018 | 0.0040 | 0.0026 | 0.0019 | 0.0010 |

a Reference [33]
b Reference [34]

FIG. 10: Binding energy discrepancies for the ArH+ molecule. The binding curves are relative to the AE UCCSD(T) binding curve. The shaded region indicates a discrepancy of chemical accuracy in either direction.

TABLE IX: Mean absolute deviations of discrepancies of binding parameters of all molecules considered in this work at equilibrium ($D_o, r_e$ and $\omega_e$) and near the all-electron dissociation threshold, $D_{diss}$ ($\lesssim 0.05$ Å), at short bond lengths for our ECPs and previous constructions with respect to all-electron UCCSD(T) calculations.

|                  | UC | SBKJC | BFD | TN-DF | STU | ccECP[Ne] | ccECP[He] |
|------------------|----|-------|-----|-------|-----|-----------|-----------|
| $D_o$ (eV/10^2)  | 1.9 | 2.4(4)| 3.4(4)| 5.1(4)| 5.9(4)| 2.6(4)    | 0.7(4)    |
| $\omega_e$ (cm⁻¹)| 6(3)| 14(3)| 9(3)| 23(3)| 12(3)| 10(3)     | 1(3)      |
| $r_e$ (mÅ)       | 16(1)| 9(1)| 14(1)| 11(1)| 17(1)| 3(1)      | 1(1)      |
| $D_{diss}$ (eV/10^2) | 16.9 | 16.9 | 31.9 | 16.5 | 38.9 | 9.6 | 1.1 |
TABLE X: Total energies of our ccECPs with [Ne] and [Ne] cores in their neutral ground states. Both RHF/ROHF and UCCSD(T) correlation energies are extrapolated to the CBS limit using the uncontracted aug-cc-pCV[T,Q,5]Z bases. Energies given in Ha.

| Atom | HF[Ne]   | Corr.[Ne] | HF[He]   | Corr.[He]   |
|------|----------|-----------|----------|-------------|
| Na   | -0.186203 | -47.577566 | -0.326840 |
| Mg   | -0.788370 | -62.911834 | -0.366702 |
| Al   | -1.875089 | -80.947812 | -0.391259 |
| Si   | -3.665501 | -101.460090| -0.431293 |
| P    | -6.344466 | -125.112316| -0.455793 |
| S    | -9.919586 | -151.257346| -0.526363 |
| Cl   | -14.741057| -181.604455| -0.583984 |
| Ar   | -20.871374| -216.492880| -0.633557 |
TABLE XI: Parameter values for Ne-core ECPs. For all ECPs, the highest \( l \) value corresponds to the local channel.

| Atom | \( Z_{	ext{eff}} \) | \( l \) | \( n_{ik} \) | \( \alpha_{ik} \) | \( c_{ik} \) |
|------|----------------|-----|----------|--------|--------|
| Na   | 9               | 0   | 2        | 29.94712200 | 221.73468900 |
|      | 1               | 1   | 11.99983500 | 9.00000000 |
|      | 1               | 3   | 11.94985400 | 107.99851500 |
|      | 1               | 2   | 12.04004600 | -69.25461900 |
| Mg   | 10              | 0   | 2        | 90.16677400 | 54.58518300 |
|      | 1               | 2   | 11.99962000 | 10.00000000 |
|      | 1               | 3   | 12.00778300 | 119.99620000 |
|      | 1               | 1   | 11.98802200 | -76.19714100 |
| Al   | 11              | 0   | 2        | 80.97577200 | 25.06358000 |
|      | 2               | 1   | 10.99788500 | 11.00000000 |
|      | 2               | 3   | 12.00778300 | 119.99620000 |
|      | 2               | 1   | 11.08325000 | -80.39326600 |
| Si   | 12              | 0   | 2        | 22.54933800 | 96.90843500 |
|      | 1               | 2   | 11.99962000 | 10.00000000 |
|      | 2               | 3   | 12.00778300 | 119.99620000 |
|      | 3               | 1   | 11.98802200 | -76.19714100 |
| P    | 13              | 0   | 2        | 54.28055538 | 35.01243588 |
|      | 0               | 2   | 34.44977221 | 155.67742201 |
|      | 1               | 3   | 12.23271871 | 152.04767654 |
|      | 2               | 2   | 12.48978664 | -103.2536836 |
| S    | 14              | 0   | 2        | 54.87912854 | 30.00006536 |
|      | 0               | 2   | 31.32968867 | 125.5010056 |
|      | 1               | 2   | 17.46806994 | 14.00000000 |
|      | 3               | 1   | 16.40968551 | 244.55297916 |
|      | 2               | 1   | 16.71492998 | -128.3775291 |
| Cl   | 15              | 0   | 2        | 44.02974125 | 202.03781785 |
|      | 0               | 2   | 65.8061305 | 25.0902536 |
|      | 1               | 1   | 20.01071281 | 15.00000000 |
|      | 2               | 3   | 21.4480478 | 300.16069215 |
|      | 2               | 1   | 21.17991361 | -151.8588234 |
| Ar   | 16              | 0   | 2        | 54.67585482 | 294.11717977 |
|      | 0               | 2   | 54.53951732 | 1.13520015 |
|      | 1               | 1   | 19.08450946 | 16.00000000 |
|      | 3               | 1   | 17.36218800 | 305.3521536 |
|      | 2               | 2   | 17.36331714 | -149.9745076 |

TABLE XII: Parameter values for He-core ECPs. For all ECPs, the highest \( l \) value corresponds to the local channel.

| Atom | \( Z_{	ext{eff}} \) | \( l \) | \( n_{ik} \) | \( \alpha_{ik} \) | \( c_{ik} \) |
|------|----------------|-----|----------|--------|--------|
| Na   | 9               | 0   | 2        | 29.94712200 | 221.73468900 |
|      | 1               | 1   | 11.99983500 | 9.00000000 |
|      | 1               | 3   | 11.94985400 | 107.99851500 |
|      | 1               | 2   | 12.04004600 | -69.25461900 |
| Mg   | 10              | 0   | 2        | 90.16677400 | 54.58518300 |
|      | 0               | 2   | 23.95808900 | 117.10269000 |
|      | 1               | 3   | 12.00778300 | 119.99620000 |
|      | 1               | 1   | 11.98802200 | -76.19714100 |
| Al   | 11              | 0   | 2        | 80.97577200 | 25.06358000 |
|      | 0               | 2   | 24.39842000 | 112.36079900 |
|      | 1               | 3   | 12.00778300 | 119.99620000 |
|      | 1               | 1   | 11.98802200 | -76.19714100 |
| Si   | 12              | 0   | 2        | 22.54933800 | 96.90843500 |
|      | 1               | 2   | 11.99962000 | 10.00000000 |
|      | 2               | 3   | 12.00778300 | 119.99620000 |
|      | 2               | 1   | 11.08325000 | -80.39326600 |
| P    | 13              | 0   | 2        | 54.28055538 | 35.01243588 |
|      | 0               | 2   | 34.44977221 | 155.67742201 |
|      | 1               | 3   | 12.23271871 | 152.04767654 |
|      | 2               | 2   | 12.48978664 | -103.2536836 |
| S    | 14              | 0   | 2        | 54.87912854 | 30.00006536 |
|      | 0               | 2   | 31.32968867 | 125.5010056 |
|      | 1               | 2   | 17.46806994 | 14.00000000 |
|      | 3               | 1   | 16.40968551 | 244.55297916 |
|      | 2               | 1   | 16.71492998 | -128.3775291 |
| Cl   | 15              | 0   | 2        | 44.02974125 | 202.03781785 |
|      | 0               | 2   | 65.8061305 | 25.0902536 |
|      | 1               | 1   | 20.01071281 | 15.00000000 |
|      | 3               | 1   | 21.4480478 | 300.16069215 |
|      | 2               | 1   | 21.17991361 | -151.8588234 |
| Ar   | 16              | 0   | 2        | 54.67585482 | 294.11717977 |
|      | 0               | 2   | 54.53951732 | 1.13520015 |
|      | 1               | 1   | 19.08450946 | 16.00000000 |
|      | 3               | 1   | 17.36218800 | 305.3521536 |
|      | 2               | 2   | 17.36331714 | -149.9745076 |
VI. CONCLUSIONS

In this work, we offer several new advances and insights into the construction of correlation consistent effective core potentials and its particular application to the second-row elements.

In certain aspects, the second row elements appear to be somewhat more complicated than the first row even though the corresponding valence spaces are very similar and the total and kinetic energies are lower (by about 20% when compared with the first row) indicating thus smoother electronic densities. Intuitively, therefore, these elements were considered “easier” than, say, describing the deeper lying and more localized p-subshells in the first row. However, the small number of valence electrons combined with larger core sizes generate more significant biases than in the first row. In particular, the core-valence effects in correlation (important for spectra) compete with the absence of electrostatic core-valence interactions (important for short bonds) and therefore these tendencies are more difficult to reconcile. We found that the fits with spectra only had limited efficiency and including more of the spatial information proved to be useful to reach the most acceptable compromises. In addition, the changes from element to element were also more significant and required a choice of optimization strategies that were adapted to particular properties of the given element.

In order to sort out these complications, we first analyzed the behavior of the one-particle HF energies together with the correlation contributions. Not too surprisingly, we found that the correlation energies for particular states and for a broad variety of existing ECPs with different parameterizations were essentially constant – the changes were on the order of 0.01-0.02 eV. This appears consistent with the key tenet of effective core potential theory that implies that the correlation will faithfully “follow” the constructed effective valence operators. However, we found this to be correct essentially only up to about 0.1 eV accuracy for atomic spectra. As soon as higher accuracy was sought and molecules were considered, the interplay between various energy components became more complicated and required refinements.

The testing of transferability proved to be very revealing. In particular, for oxide molecules at short bond lengths, we see a significant departure from the assumed accuracy standards of ≈ 0.05 eV for both ours and existing ECPs for elements in the middle such as Al and Si. We traced the deficiency to the missing electron core tails and likely core-valence effects which are absent in the ECP and would need to be included to reach higher accuracies. Similar problems have been noticed before, see for example, Ref. [37]. Here we present a systematic view on this issue for oxide molecules and, in addition, we point out that elimination of this issue might require more elaborated solutions. (We have tested the inclusion of classical effective repulsive charges that would correspond to the electronic core-core interactions that could reasonably restore the desired accuracy. In order to introduce this in a more thought-through fashion, we leave this aspect for future studies.) This is a notable point that can affect many oxide calculations such as Al and Si perovskites at high pressures (for example, these are important components of the Earth’s mantle). Due to the importance of oxides, it is highly desirable to probe for these particular aspects in calculations of solids and other systems.

The atomic spectra and Tab. IX show that apart from the inherent bias for a few short polar bonds our constructions show consistent accuracy in both atomic and molecular calculations and offer close to an optimal balance overall. Our results, somewhat unexpectedly, are on par or in a few cases significantly improve upon the ECPs from the SBKJC table. Except for the Na atom (which is a bit special having only one valence electron), SBKJC ECPs appear to represent perhaps the most systematic consistency among the tested previous constructions. Note that the SBKJC ECPs are not bound at the nucleus, diverging as 1/r² in repulsive and −Z_{eff}/r in the local channels. Due to our choice of the ccECP form with bounded potentials and minimized radial extent of the nonlocal terms (although not explicitly enforced) for several elements we just hit similar or comparably optimal point as has been achieved in SBKJC table before. In some cases, we were able to actually find significantly better compromises. As mentioned before, we note that Ne-core ECPs for atoms such as Na and Mg with one or two valence electrons might prove to have only limited applicability in some bonding environments where shallow core states contribute to the chemical effects (for example, in compounds at high pressures).

It is also clear that core polarization and relaxation potentials [38–41] can alleviate some of the mentioned deficiencies. In this study, however, we first wanted to see the limits of the simplest ECP form before employing new terms. In addition, oxide molecules for elements in the middle might be difficult to “fix” since the root of the problem appears to be the missing repulsive (essentially classical) charge from core electrons and this might require a more general and more extensive modification of the ECP form.

On the other hand, since we report here on the existing limits of the Ne-core ECPs in their current forms, we have decided to provide another option for high accuracy calculations that offer a significant boost in accuracy and eliminate many compromises mentioned above. To this end, we constructed high accuracy He-core ECPs that significantly decrease the discrepancies with all-electron relativistic calculations. The gain is by an order of magnitude or more, with typical errors of 0.001-0.005 eV on the atomic side and ≈ 0.01 eV for molecular systems. Obviously, these operators imply additional cost that is most pronounced in stochastic methods due to the increase of total energies and fluctuations. Note that some of that is compensated from much smaller effective core radius of nonlocal terms [42].
Overall, we believe that the constructed ECPs provide both new insights as well as practical new options for high accuracy valence-only calculations. Supplementary material contains further information such as corresponding basis sets as well as very accurate exact, many-body total energies (better than 1 mHa accuracy) for atomic states. The potentials and basis sets are also accessible at the website [http://pseudopotentiallibrary.org](http://pseudopotentiallibrary.org). Besides this data, the presented analysis offers a clear comparison between existing ECPs and should open new perspectives for further advances in this important research area.
Acknowledgements

We would like to thank P. Kent for reading the manuscript and for suggestions. The majority of this work (development of the methods, calculations, tests, and writing of the paper) has been supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Sciences and Engineering Division, as part of the Computational Materials Sciences Program and Center for Predictive Simulation of Functional Materials. The initial theoretical and conceptual considerations were supported by ORNL/UT Battelle, LLC, subcontract N. 4000144475.

The calculations for this work were performed mostly at Sandia National Laboratories, while some of the calculation have been carried out at TACC under XSEDE.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia LLC, a wholly owned subsidiary of Honeywell International Inc. for the U.S. Department of Energys National Nuclear Security Administration under contract de-na0003525.

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