Pseudopotential contributions to the quadrupole moment in charged periodic systems

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There has been much interest over many years in studying charged systems after the artificial imposition of periodic boundary conditions, and correcting for the resulting divergence of the electrostatic energy density. A correction for cubic cells was derived by Makov and Payne in 1995, and its leading error term is of the form L^{-5} for a cube of side L. Most modern density functional theory codes use a different treatment of the $Z\alpha$ energy term to that used by Makov and Payne, resulting in an error term of the form L^{-3} if their correction is used unmodified. This paper shows how the Makov and Payne result can be made consistent with modern practice.

I. INTRODUCTION

Many density functional theory codes assume three-dimensional (3D) periodicity, which enables the use of simple techniques such as plane waves for the basis set, and the 3D Ewald sum for electrostatic interactions. ABINIT [1], CASTEP [2], QUANTUM ESPRESSO [3], VASP [4], and others use this approach.

If the system to be modeled is not periodic in all three dimensions, then it can be repeatedly tiled to generate periodicity, with a vacuum region separating the repeated images. Ideally the calculated energy, and other quantities of interest, converge rapidly as the size of the vacuum region is increased.

If the system of interest has zero net charge and no dipole moment, convergence is reasonably rapid. The worst convergence arises for systems with net charge, for which the uncorrected energy per unit volume is divergent. The Ewald sum automatically removes this divergence by introducing a uniform compensating charge density to neutralize the cell, but it leaves other terms, which are slow to converge.

The issue was addressed by Makov and Payne [5] who proposed a two-term correction to the energy for cubic cells. The first term scales as $1/L$ (where L is the cell length), and is simply the Madelung energy of the lattice. The second scales as L^{-3} and depends on the total charge and on the scalar quadrupole moment, Q, (also known as the trace of the quadrupole moment tensor) defined as

$$Q = \int_{\text{cell}} r^2 \rho(r) d^3r, \qquad (1)$$

where $\rho(r)$ is the charge density.

Such corrections, in various geometries, remain the subject of current research [6–8]. Historically corrections for charged systems have been achieved by adding extra terms to the energy, as Makov and Payne did. They may also be achieved

by adding a constant to the potential so that its average value is no longer zero [9].

Studies of charged defects in bulk materials need to address further complications such as the convergence of elastic deformation energies with cell size, potentially poor localization of the charge invalidating expansions based on point multipoles, including the Madelung energy, and the need to consider the relative permittivity of the bulk. Such issues produce terms in the energy decaying as slowly, or more slowly, than the inverse of the volume and prevent even the $1/L$ energy scaling from being fully corrected [10,11]. Furthermore, Q is not well defined in periodic systems, being origin dependent even in the absence of both a net charge and dipole moment. The value of Q per unit cell depends on the precise boundary conditions at infinity. This paper is restricted to isolated charged ions so as to avoid the many complications introduced by bulk systems.

A pseudopotential differs from the corresponding Coulomb potential within the pseudopotential's core radius. Thus the integral of the pseudopotential's potential over all space may differ from that of a Coulomb potential too. Both integrals are infinite, but their difference is well defined. The difference is called the non-Coulomb $g = 0$ term of the pseudopotential, and is usually denoted by α [12]. It appears in the expression for the total energy as

$$E = \frac{|Z|}{V} \sum \alpha_i, \qquad (2)$$

where the sum is over all atoms present, V is the cell volume, and Z is the total charge. Once the system has a net charge, the total electronic charge and the total ionic charge differ, so it matters which is used. It had been conventional to use the total electronic charge [13,14], but more recent work [9] has shown that the total ionic charge is better justified, and this later convention is now widely adopted. In some sense both are correct, for once one tries to reduce an infinite energy, the energy per unit cell of a 3D-periodic charged system, to a finite value, the resulting finite value will depend on the conventions used for the reduction.

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II. A PSEUDOPOTENTIAL'S QUADRUPOLE MOMENT

A dipole, p, consisting of two equal and opposite charges of magnitude p/r_0 separated by a distance r_0 produces a potential, which extends to infinity. The integral of that potential over all space is zero if one integrates over the volume of a sphere centered on the center of the dipole. This can be seen by considering the symmetry operation of changing the sign of all the charges, which must change the sign of the integral, followed by a rotation to make the sign-changed system identical to the old, an operation which will have no effect on the integral.

A similar argument applies to a quadrupole moment consisting of alternating charges arranged on the corners of a square. But a quadrupole is a tensor, and not all of its components can be represented thus. The scalar quadrupole moment, Q, described by Eq. (1), is represented by a spherical shell of charge of radius r_0 and magnitude Q/r_0^2 together with a compensating central point charge of magnitude $-Q/r_0^2$.

At radii greater than r_0 a spherical Gaussian surface contains no net charge, and, by symmetry, can have no field. Assuming that the potential is zero at infinity, it is zero at all radii $> r_0$. For radii less than r_0, the point charge produces the usual $1/r$ potential, and the spherical shell a constant potential given by the value for a point charge at r_0. One can determine the integral of the total potential given by this model of a quadrupole:

$$\int_0^\infty \phi(r)d^3r = \int_0^{r_0}\left(\frac{Q}{4\pi\epsilon_0 r_0^3} - \frac{Q}{4\pi\epsilon_0 r_0^2 r}\right)4\pi r^2 dr \quad (3)$$

$$= \frac{Q}{\epsilon_0}\left[\frac{r^3}{3r_0^3} - \frac{r^2}{2r_0^2}\right]_0^{r_0} \quad (4)$$

$$= -\frac{Q}{6\epsilon_0}. \quad (5)$$

In other words, a scalar quadrupole moment Q will change the integrated value of the electrostatic potential by an amount $\frac{-Q}{6\epsilon_0}$. In the limit of $r_0 \to 0$ a point quadrupole moment produces no field, but acts as a delta function addition to the potential. If the average potential of a system is fixed, and the Ewald summation fixes it to zero by ignoring the $g = 0$ Fourier components, then the addition of such a quadrupole moment produces a shift of the potential throughout the cell.

This is analogous to the α term of a pseudopotential, which represents how the integral of the local part of the pseudopotential differs from that of the corresponding Coulomb potential. The ion-ion interaction term in the total energy is accounted for in the Ewald sum, which assumes that the ions are outside of each others' pseudopotential core radii, and thus in the region where the pseudopotentials are identical to Coulomb potentials. But if one is setting the average potential to zero, then the α term produces a shift in the potential outside the core radius, and this leads to the $Z\alpha$ energy term identified by Ihn [12] and repeated here as Eq. (2).

III. MAKOV-PAYNE CORRECTION FOR CHARGED SYSTEMS

The basic expression for the energy of a system in density functional theory is given by

$$E = E_k + E_{ee} + E_{\text{Ewald}} + E_{ie} + E_{XC} + \frac{|Z|}{V}\sum\alpha_i, \quad (6)$$

where E_k is the kinetic energy of the electrons, E_{ee} is the Hartree energy, describing the Coulomb part of the electron-electron interaction, E_{Ewald} is the Ewald energy describing the ion-ion Coulomb interaction, E_{ie} is the Coulomb interaction between the electrons and the ions, E_{XC} is the exchange-correlation energy. Finally there is the $Z\alpha$ term of Eq. (2). It arises because each of E_{ee}, E_{Ewald}, and E_{ie} is infinite, with the infinities arising from the dc component of the potential in Fourier space. In a neutral system these infinities cancel, and numerically this cancellation is achieved by setting the average value of the each potential to zero. The ionic potential is treated as Coulombic in the Ewald energy, but as arising from the ions' pseudopotentials in the E_{ie} term. Given that an ion's pseudopotential and Coulomb potential are identical outside of the pseudopotential's core radius, and that the core radius should be sufficiently small that no other ion lies within it, this would appear not to matter. But because the integrated potential is set to zero, and the integrals of the Coulomb and pseudopotentials differ, it leads to a relative shift of the two potentials, which is then corrected by the final $Z\alpha$ term.

To this may be added corrections for the long-ranged effects of dipoles and net charges. The energy correction for charged systems proposed by Makov and Payne for a charged system in a cubic cell [5] is

$$-\frac{q^2 M}{8\pi\epsilon_0 L} - \frac{qQ}{6\epsilon_0 V}, \quad (7)$$

where q is the net charge, M the Madelung constant of the lattice, Q the total quadrupole moment, L the side length of the cube, and $V = L^3$ the cell volume. They demonstrated that this correction removed terms decaying slower than L^{-5}, and they used the total electronic charge in Eq. (2). The first term, the Madelung energy, was well known, but the second quadrupole term was novel.

For a charged system, it matters whether the Z in the final term of Eq. (6) refers to the total electronic charge, as was conventional when the Makov and Payne paper was written, or the total ionic charge, as is conventional now. So to reproduce their work it is necessary to consider the $Z\alpha$ term in conjunction with the quadrupole term from Eq. (7).

On adding their $Z\alpha$ term to their quadrupole term one obtains

$$E_{MP} = -\frac{qQ}{6\epsilon_0 V} + \frac{Z - q}{V}\sum\alpha_i \quad (8)$$

with Z as the total ionic charge, and thus $Z - q$ the total electronic charge as used in their $Z\alpha$ term. This can be rearranged to produce the current $Z\alpha$ term by writing

$$E_{MP} = -\frac{q(Q + 6\epsilon_0\sum\alpha_i)}{6\epsilon_0 V} + \frac{Z}{V}\sum\alpha_i. \quad (9)$$

Their total quadrupole moment, Q, was obtained by applying Eq. (1) to the valence charge density coupled with the

ions considered as point charges. Suppose that the pseudopotentials themselves have some sort of intrinsic quadrupole moment Q_{ps} that should also be considered, so that in place of Q one should write $Q + \sum Q_{ps,i}$. If $Q_{ps,i}$ is defined to be $6\epsilon_0\alpha_i$ then Eq. (9) follows immediately.

Thus the Z in the $Z\alpha$ term has been restored to modern convention of the total ionic charge by considering the spherical quadrupole moment in the Makov-Payne correction to include an extra term arising from the 'quadrupole moments' of the pseudopotentials.

So one can either use the Makov-Payne correction with their definition of the system's quadrupole moment and their use of the total electronic charge in the $Z\alpha$ term, or equivalently one can add the pseudopotential's scalar quadrupole moments, defined as above in terms of α, to the system's quadrupole moment, and follow the convention of using the total ionic charge in the $Z\alpha$ term.

It should be noted that this identification of the α term of a pseudopotential with a quadrupole moment is not helpful in calculating the scalar quadrupole moment of a system. To do that accurately one needs the correct charge density within the pseudopotential's core radius.

IV. RECONSTRUCTING A CHARGE DENSITY

An alternative approach might consider reconstructing the charge density that would give rise to the pseudopotential. To do so using just Gauss's law, and thus ignoring the XC potential, is a very artificial approach, but it does yield a useful result.

Pseudopotentials are spherically symmetric, so the total charge within a given radius, $q(r)$, is given by

$$q(r) = \int_0^r \rho(r')4\pi r'^2 dr', \tag{10}$$

where ρ is the charge density and ϕ the potential, and with $q(r_c)$ being the total charge on the pseudopotential.

Gauss's law is

$$\rho = -\epsilon_0 \nabla^2 \phi \tag{11}$$

$$= -\epsilon_0 \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial \phi}{\partial r}\right), \tag{12}$$

which can be inverted as

$$\phi(r) = \int_r^\infty \frac{1}{r'^2}\int_0^{r'} \frac{s^2\rho(s)}{\epsilon_0}ds\,dr' \tag{13}$$

$$= \int_r^\infty \frac{1}{r'^2}\frac{q(r')}{4\pi\epsilon_0}dr'. \tag{14}$$

The scalar quadrupole moment of the charge distribution is defined as follows:

$$Q = \int_0^{r_c} r'^2 \rho(r')4\pi r'^2 dr' \tag{15}$$

$$= [r^2 q(r)]_0^{r_c} - 2\int_0^{r_c} rq(r)dr \tag{16}$$

$$= r_c^2 q(r_c) - 2\int_0^{r_c} rq(r)dr, \tag{17}$$

where integration by parts, and Eq. (10), move from the standard definition to the final form. And α, the difference between the integral of the pseudopotential, $\phi(r)$, and the integral of a Coulomb potential from the same charge, is defined [13,14] as

$$\alpha = \int_0^{r_c}\left(\frac{q(r_c)}{4\pi\epsilon_0 r'} - \phi(r')\right)4\pi r'^2 dr' \tag{18}$$

$$= \frac{1}{\epsilon_0}\int_0^{r_c}\left(q(r_c)r' - r'^2\int_{r'}^\infty \frac{q(s)}{s^2}ds\right)dr'. \tag{19}$$

The second part of the integral may be done by parts, and the $q(r_c)$ term is integrated directly.

$$\alpha = \frac{1}{\epsilon_0}\left(\frac{q(r_c)r_c^2}{2} - \left[\frac{r'^3}{3}\int_{r'}^\infty \frac{q(s)}{s^2}ds\right]_0^{r_c} - \int_0^{r_c}\frac{r'^3}{3}\frac{q(r')}{r'^2}dr'\right) \tag{20}$$

$$= \frac{1}{\epsilon_0}\left(\frac{q(r_c)r_c^2}{2} - \left[\frac{r'^3 q(r_c)}{3}\int_{r'}^\infty \frac{1}{s^2}ds\right]_0^{r_c}\right.$$
$$\left. - \frac{1}{3}\int_0^{r_c} r'q(r')dr'\right) \tag{21}$$

$$= \frac{1}{\epsilon_0}\left(\frac{q(r_c)r_c^2}{2} - \left[\frac{r'^3 q(r_c)}{3r'}\right]_0^{r_c} - \frac{1}{3}\int_0^{r_c} r'q(r')dr'\right) \tag{22}$$

$$= \frac{1}{6\epsilon_0}\left(q(r_c)r_c^2 - 2\int_0^{r_c} r'q(r')dr'\right) \tag{23}$$

$$= \frac{Q}{6\epsilon_0}. \tag{24}$$

Noting that $q(r) = q(r_c)$ for all $r \geqslant r_c$, and substituting from Eq. (17) for the last line.

So we conclude that the scalar quadrupole moment of a charge distribution, which, though simple electrostatics, gives rise to a pseudopotential with a given α term is $Q = 6\epsilon_0\alpha$. Whereas Eq. (5) showed that a scalar quadrupole moment gives this integrated potential, Eq. (24) gives the more general result that Q and α obey this relationship for any potential arising from a spherically symmetric charge density.

V. IONIZATION ENERGY OF Mg

An example used by Makov and Payne in their paper introducing this correction was the ionization energy of Mg. They calculated the energy difference between Mg and Mg$^+$ in cubic boxes with sides ranging from 9 Å to 13 Å. These calculations are now repeated to show the difference between using just a Madelung energy correction, adding the quadrupole correction in the form described by their paper, and adding it in the form described here with the quadrupole moment including a $6\epsilon_0\alpha$ term. A norm-conserving Mg^{2+} pseudopotential and the LDA XC functional were used, as they would have done. CASTEP [2] was used, and C2X [15] to calculate the quadrupole moment in a postprocessing step. Figure 1 repeats their figure 3(b), but a range of 9 Å to 20 Å is used.

The energies after the Madelung correction differ. Theirs converge from below, whereas the results in this paper converge from above. This is to be expected, as the different treatment of the Z in the $Z\alpha$ term means that these calculations
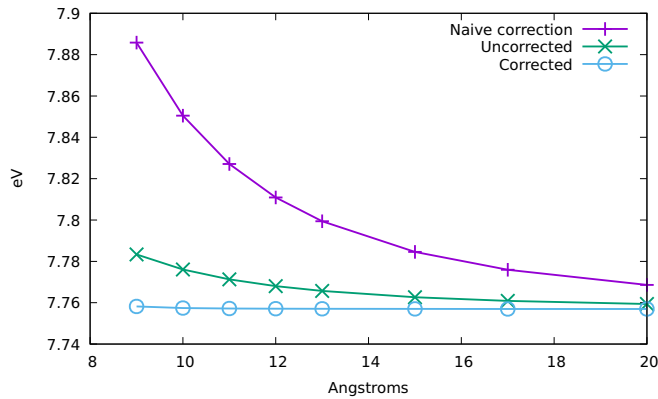
FIG. 1. The ionization energy of magnesium, calculated in cubic boxes of increasing side length. All energies are shown after a simple Madelung correction. Those labeled uncorrected have no further correction, those labeled naively corrected also have the Makov-Payne correction naively applied to the output of a modern DFT code, and those labeled corrected have the Makov-Payne correction correctly applied.
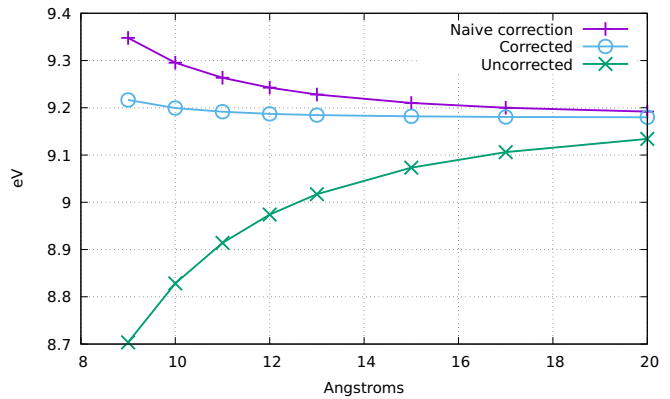

FIG. 2. The ionization energy of benzene, calculated in cubic boxes of increasing side length, in the same manner as Fig. 1. All energies are shown after a simple Madelung correction. Two further curves show the result of applying the Makov-Payne correction naively to the output of a modern DFT code, and applying it correctly.

are not identical. This is the reason why the correction they proposed no longer works in the precise form they gave. The experimental value of the ionization energy of Mg is 7.646 eV [16], and even this simple calculation, which yields 7.76 eV is quite close, and closer than Makov and Payne's 1995 result of around 7.95 eV. Pseudopotential improvements may account for the difference. Repeating the calculations with a more modern XC functional, PW91 [17], produces a result of 7.66 eV.

The calculated scalar quadrupole moment of the electron density in the Mg^+ system is around -2.45 eÅ^2. The norm-conserving pseudopotential generated by CASTEP has an α corresponding to a quadrupole moment of $+3.08$ eÅ^2. Thus the electronic quadrupole moment has the opposite sign to the total moment produced by including the $6\epsilon_0\alpha$ term from the pseudopotential, and a naive attempt to use the quadrupole term from the Makov-Payne correction results in a correction of the wrong sign, which makes the error worse. In this example, the unmodified correction uses a quadrupole moment of -2.45 eÅ^2 whereas it should use $+0.63$ eÅ^2, so the unmodified correction is almost four times too large, as well as having the wrong sign.

VI. IONIZATION ENERGY OF BENZENE

As a second example the ionization of benzene is considered. The benzene ion differs from Mg^+ in some important aspects. It is not spherically symmetric, and it is much larger, with the charge delocalized across the whole ion. Thus it fits less well with a theory based on point multipole expansions. Relaxation of the atomic positions was not performed.

The sum of the α terms of the pseudopotentials generated by CASTEP corresponds to a quadrupole moment of $+3.2$ eÅ^2, and the scalar quadrupole moment of the ions considered as point charges, plus the electron density, is around -15.3 eÅ^2. So now a naive attempt to use the Makov-Payne correction results in a correction of the correct sign, but overestimates the magnitude by about a quarter, for the correct total quadrupole

moment including the contribution from the pseudopotentials is around -12.1 eÅ^2, but ignoring the pseudopotential term gives rise to a larger moment of -15.3 eÅ^2, and hence an erroneously large Makov-Payne correction.

Figure 2 shows the result of applying the Makov-Payne correction as a *post hoc* energy correction both with, and without, considering the contributions of the pseudopotentials to the quadrupole moment. Although convergence for this more extended system is slower than for the Mg^+ ion, the correction is still very helpful.

Ideally such corrections are applied self-consistently, rather than in a *post hoc* fashion. The extra energy term, which depends on the quadrupole moment ought to be considered as giving rise to a potential, which acts on the electrons so as to penalize configurations that lead to energetically unfavorable moments. This was not done, and the omission results in a quadrupole moment that varies slightly with cell size. The moment excluding the pseudopotentials varied from -15.57 eÅ^2 in a 9 Å cell to -15.27 eÅ^2 in the 20 Å cell.

Setting the zero frequency Fourier component of the charge density to zero, as is necessary to prevent the energy per unit cell diverging, is equivalent to introducing a uniform neutralizing background charge, often called jellium. This produces an unwanted potential. The density of the jellium is $-q/V$ where q is the net charge of the cell and V its volume. The potential, ϕ, which arises can be obtained from Gauss's law if one assumes that the potential is spherically symmetric. This assumption should be approximately valid close to the center of the cubic cell.

$$\nabla^2\phi = \frac{q}{\epsilon_0 V} \tag{25}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\phi}{\partial r}\right) = \frac{q}{\epsilon_0 V} \tag{26}$$

$$\phi = \frac{qr^2}{6\epsilon_0 V}. \tag{27}$$

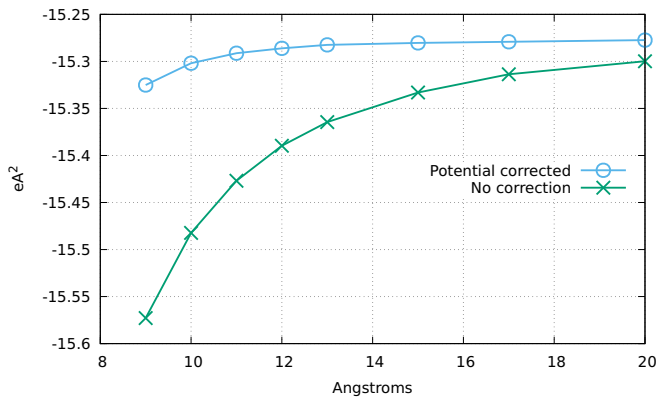This result immediately gives the Makov-Payne energy correction, for the energy of a quadrupole moment, Q, in

FIG. 3. The scalar quadrupole moment of the benzene ion, calculated in cubic boxes of increasing side length. Moments are show before and after applying a correcting quadratic potential to compensate for the potential arising from the uniform density of the background jellium.

this potential is $qQ/6\epsilon_0 V$, and this unwanted energy term needs subtracting from the energy obtained when jellium is included, just as this unwanted potential needs subtracting. This term is also given by Komsa *et al.* [11] in their equation 20.

The difference in the convergence of the energy between using a *post hoc* correction, and correcting the potential within the calculation, is slight. In a cell of side 9 Å, the error in the energy after the *post hoc* correction is about 36 meV, and with the corrected potential this error is reduced by about 5 meV. The difference is more marked in the calculated quadrupole moment, and this is shown in Fig. 3. Without the correction, the quadrupole moment converges with a leading error term inversely proportional to volume, and with it the leading error term appears to be inversely proportional to the square of the volume.

VII. EIGENVALUES OF BENZENE

Not only should the total energy of an isolated charged system converge rapidly with increasing simulation cell size,

and also its charge density and the moments thereof, but so too should the eigenvalues of the electronic bands. The *post hoc* energy correction of Makov and Payne makes no attempt to adjust the eigenvalues, but they can be corrected by making a corresponding correction to the potential. As given by Komsa *et al.* [11], this is

$$\phi_{MP} = \frac{q\alpha}{4\pi\epsilon_0 L} - \frac{Q}{6\epsilon_0 V} - \frac{qr^2}{6\epsilon_0 V}. \qquad (28)$$

The same expression is also given by Dabo *et al.* [18,19], save that they did not choose their origin to set the dipole moment equal to zero.

The last of these terms was introduced in the previous section. The other two are constants, so may be implemented as a *post hoc* shift to the eigenvalues. The middle term contains Q, and again the quadrupole moment including the contributions from the pseudopotentials should be used.

As an illustration, the benzene ion is again chosen. The eigenvalue considered is that of the highest (partially) occupied band when the charge is $+\frac{1}{2}$, which is a value expected to approximate to the ionization energy [20].

The left-hand part of Fig. 4 shows the slow convergence of the eigenvalue when no corrections are applied, and the much better convergence when simply the first Madelung constant shift is added. The right-hand part shows again the results after applying the Madelung correction, but also after applying the second term of the correction in a *post hoc* fashion. To produce this figure, it was assumed that the electronic and ion point charge contribution to Q was -18.27 eÅ^2, its value in the 20 Å cube, and the pseudopotential contribution was $+3.18$ eÅ^2 so the correct value for Q was -15.09 eÅ^2.

With no correction the convergence is very slow, the leading term in the error being of the form $1/L$. Adding the Madelung correction greatly improves the convergence, with the leading error term becoming $1/V$. Ignoring the pseudopotentials' moments when adding the next correction term leads to overcorrection, whereas including them gives very good convergence. For these calculations the r^2 term of Eq. (28) was included in all four cases. The ionization energy predicted by this method of 9.29 eV does not quite agree with the 9.18 eV of the previous section, but this method produces
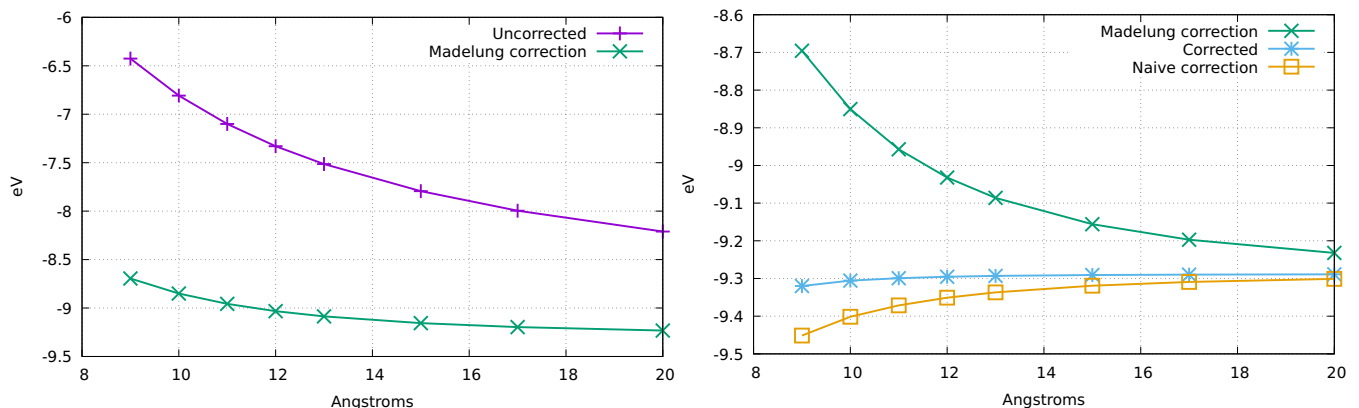

FIG. 4. The left-hand graph shows the convergence of the highest occupied eigenvalue of benzene with a $\frac{1}{2}$ positive charge. It is shown with no corrections, and with the Madelung correction. The right-hand graph repeats the Madelung-corrected curve, but then adds the quadrupole correction with the pseudopotentials' quadrupole moments excluded, labeled naive, and included, labeled corrected.

estimates, not exact results. For the purposes of this discussion, it is the improved convergence with cell size, which is of note.

VIII. CONCLUSION

While the quadrupole correction for charged periodic systems proposed by Makov and Payne appears to be incorrect when combined with more recent treatments of the non-Coulomb pseudopotential energy term, it can be corrected by assuming that the pseudopotentials themselves have scalar quadrupole moments. Not only is this physically consistent with the concept of a pseudopotential replacing a cloud of core electrons, which would have a quadrupole moment, but the required magnitude of the moment can be obtained by an analytical calculation on a simple model. To use the correction of Makov and Payne in codes that use the total ionic charge

in their $Z\alpha$ energy term, a correction equivalent to reverting to the total electronic charge in the $Z\alpha$ term is required, and this can be achieved by equating the pseudopotential's α to a quadrupole moment. Failure to make this adjustment can lead to the quadrupole term of the Makov-Payne correction having not just the wrong magnitude, but also the wrong sign and so increasing the error.

This observation is extended to the corrections to the potential implied by the Makov and Payne correction. Including a contribution from the pseudopotentials in the calculation of the quadrupole moment greatly improves the convergence of the eigenvalues.

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