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Communication: Finite size correction in periodic coupled cluster theory calculations of solids

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We present a method to correct for finite size errors in coupled cluster theory calculations of solids. The outlined technique shares similarities with electronic structure factor interpolation methods used in quantum Monte Carlo calculations. However, our approach does not require the calculation of density matrices. Furthermore we show that the proposed finite size corrections achieve chemical accuracy in the convergence of second-order Møller-Plesset perturbation and coupled cluster singles and doubles correlation energies per atom for insulating solids with two atomic unit cells using $2 \times 2 \times 2$ and $3 \times 3 \times 3$ k -point meshes only. *Published by AIP Publishing*. [<http://dx.doi.org/10.1063/1.4964307>]

I. INTRODUCTION

Correlated wave function based methods are a promising tool for the accurate solution of the many-electron Schrödinger equation on an *ab initio* level. However, in contrast to computationally much cheaper mean-field theories, these methods are limited in terms of applicability due to their relatively large computational cost.^{1–4} Moreover the relatively large computational cost gets further increased in practice by the slow convergence of calculated properties with respect to the treated system sizes. Many properties such as the binding energy of molecules on a surface converge slower than their counterparts calculated using mean-field theories. This originates from the fact that correlated wave function based theories capture more longer ranged electronic correlation effects such as dispersion interaction explicitly. Therefore it is important to develop methods that improve the rate of convergence.

Quantum Monte Carlo (QMC) calculations of solids also suffer from a slow convergence of calculated properties with respect to the treated system sizes. However, QMC methods employ correction schemes to reduce the finite size errors originating from the evaluation of the kinetic and potential energy operators in the many-electron Hamiltonian.^{5–7} The most notable corrections include structure factor interpolation techniques and twist-averaging. The latter is employed to reduce finite size errors originating from the one-electron operators. In passing we note that these errors can often be kept very small in quantum chemical (QC) wave function based theory calculations because the corresponding energy contributions can already be captured to a large extent on the level of Hartree–Fock (HF) theory. On the other hand, finite size errors originating from the two-electron operator are equally problematic in QMC and QC calculations of solids. These errors can successfully be reduced using electronic structure factor interpolation methods.

In this work, we will outline a similar approach to the electronic structure factor interpolation method that is suitable for correlated quantum chemical wave function based theories in solids. We will show that the proposed technique does not require the prior calculation of any density matrices as needed for the calculation of the electronic structure factor. Furthermore the method is also capable of achieving rapidly convergent electronic correlation energies for insulating solids.

II. THEORY

In coupled cluster theory calculations, the total energy is usually expressed as a sum of the Hartree–Fock energy and the coupled cluster correlation energy, calculated from the Hartree–Fock orbitals. The coupled cluster singles and doubles (CCSD) correlation energy can be written as²

$$E_c = \sum_{ij} \sum_{ab} T_{ij}^{ab} W_{ij}^{ab}, \quad (1)$$

where $T_{ij}^{ab} = t_{ij}^{ab} + t_{ij}^{ab}$ and $W_{ij}^{ab} = 2V_{ij}^{ab} - V_{ij}^{ba}$. t_i^a and t_{ij}^{ab} are singles and doubles amplitudes obtained from solution of the corresponding amplitude equations.² The indices i, j and a, b are understood to be shorthands for the spatial orbital index and the Bloch wave vector. The two-electron integrals are calculated using $V_{ij}^{ab} = \sum_{\mathbf{G}} C_i^a(\mathbf{G}) v(\mathbf{G}) C_j^{b*}(\mathbf{G})$, where $C_i^a(\mathbf{G})$ is defined by $\sum_{\mathbf{G}} C_i^a(\mathbf{G}) e^{i\mathbf{G}\mathbf{r}} = \phi_i(\mathbf{r}) \phi_a^*(\mathbf{r})$.^{8–11} We stress that the orbital overlap charge density $\phi_i(\mathbf{r}) \phi_a^*(\mathbf{r})$ is approximated in the projector augmented wave method using Eq. (2.87) of Ref. 12 as implemented in the Vienna *ab initio* simulation package (VASP).^{13–15} The Coulomb kernel in reciprocal space is defined as $v(\mathbf{G}) = \frac{4\pi}{\mathbf{G}^2}$. \mathbf{G} corresponds to the sum of a Bloch wave vector and a reciprocal lattice vector. In this work, we will only consider Γ -centered k -point meshes.

The expression for the correlation energy can be rewritten by rearranging the nested summations in Eq. (1) and the

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definition of W_{ij}^{ab} such that

$$E_c = \sum_{\mathbf{G}}' v(\mathbf{G})S(\mathbf{G}), \quad (2)$$

where $S(\mathbf{G}) = \sum_{ij} \sum_{ab} T_{ij}^{ab} (2C_i^a(\mathbf{G})C_b^{j*}(\mathbf{G}) - C_i^b(\mathbf{G})C_a^{j*}(\mathbf{G}))$. Equation (2) is a central equation for the present work. We stress that $S(\mathbf{G})$ depends only linearly on the doubles amplitudes and does not correspond to the electronic structure factor. The apostrophe indicates that the sum in Eq. (2) includes only plane wave vectors for which $G_{\min} \leq |\mathbf{G}| \leq G_{\max}$ holds. We note that G_{\max} corresponds to a plane wave vector cutoff. G_{\min} is the length of the shortest plane wave vector included in the basis set that is not equal to zero. In the following, we will discuss finite size and finite basis set errors with the help of G_{\min} and G_{\max} , respectively.

The finite basis set error vanishes only in the limit of $G_{\max} \rightarrow \infty$.¹⁶ This observation is not surprising since the leading order basis set error originates from the so-called electron-electron cusp conditions, which are in real space a short-ranged electronic correlation phenomenon. Explicitly correlated methods help in reducing the finite basis set error substantially.^{17,18} These methods as well as their application to periodic systems have already been discussed elsewhere.^{11,19,20}

Finite size errors vanish in the limit of employing increasingly dense k -point meshes in the calculation of solids, concomitantly reducing G_{\min} . These errors originate from the neglect of long range electronic correlation effects such as van der Waals type interactions.^{21–23} Numerically it has been shown that second-order Møller-Plesset (MP2) and coupled cluster correlation energies of periodic solids converge as $1/M_k$ to the thermodynamic limit, where M_k refers to the total number of k -points used to sample the first Brillouin zone.^{4,24,25}

We now return to Eq. (2) and seek to discuss the function $S(\mathbf{G})$ in greater detail. To this end we have calculated $S(\mathbf{G})$ using coupled cluster singles and doubles theory for the carbon diamond crystal. Figure 1 shows $S(\mathbf{G})$ retrieved as a function of $|\mathbf{G}|$ for several k -point meshes $N_k \times N_k \times N_k$, where $N_k = 1, 2, 3$, and 4. Numerically we find that $S(\mathbf{G})$ decays to zero for $|\mathbf{G}| \rightarrow 0$ and $|\mathbf{G}| \rightarrow \infty$. We note that $S(\mathbf{G})$ exhibits two relevant properties. First, $S(|\mathbf{G}|)$ is not a smooth function due to the anisotropy of the diamond structure. Second, $S(|\mathbf{G}|)$ converges rapidly with respect to N_k in particular for long plane wave vectors. From the latter we conclude that the dominant finite size error originates from the region close the Coulomb singularity in reciprocal space, which is neglected in the summation in Eq. (2) for coarse k -point meshes.

We now discuss the reason for the asymptotic behaviour of the correlation energy with respect to M_k . The vertical lines in Fig. 1 depict that G_{\min} reduces as the employed k -point mesh sampling density increases. We stress that $S(\mathbf{G})$ and $v(\mathbf{G})$ converge to zero and ∞ in the limit $G \rightarrow 0$, respectively. A Taylor series expansion of $S(\mathbf{G})$ around $\mathbf{G} = 0$ reveals that the leading order nonzero term becomes $\propto \mathbf{G}^2$. Note that all terms linear in \mathbf{G} vanish as a result of $C_i^a(0) = 0$ because of the orthogonality between occupied and unoccupied orbitals.

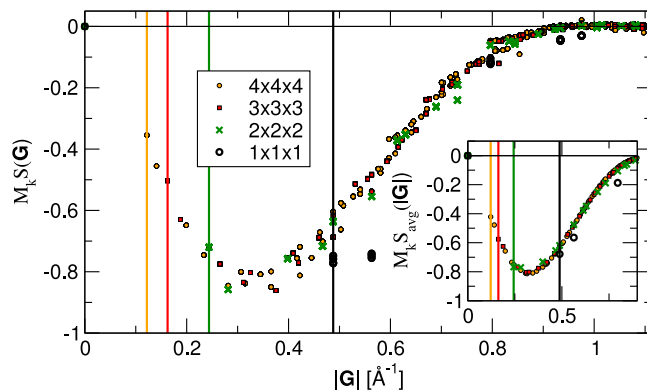


FIG. 1. The convergence of $M_k S(\mathbf{G})$ for the carbon diamond crystal for a range of k -point meshes including $1 \times 1 \times 1$, $2 \times 2 \times 2$, $3 \times 3 \times 3$, and $4 \times 4 \times 4$. The vertical lines indicate the respective values for G_{\min} . The CCSD calculations have been performed using 32 orbitals per k -point. The vertical axis has been rescaled. The sum over plane wave vectors has been restricted to all plane waves with a kinetic energy below 400 eV. The inset shows $M_k S_{\text{avg}}(|\mathbf{G}|)$ using the same system and settings.

Therefore $S(\mathbf{G})v(\mathbf{G})$ approaches a constant number at $|\mathbf{G}| = 0$. Due to this and the discretisation of the integration over \mathbf{G} in Eq. (2), the contribution from the sampling point at $\mathbf{G} = 0$ decays as $\frac{1}{M_k}$. This explains the $1/M_k$ asymptotic behaviour of the correlation energy. However, we note that computationally it is difficult to use sufficiently dense k -point meshes to observe a quadratic behavior in $S(\mathbf{G})$. For coarse k -point meshes, the retrieved function in Fig. 1 exhibits a linear behaviour around G_{\min} , indicating that the quadratic term starts to dominate only for very small \mathbf{G} vectors corresponding to $3 \times 3 \times 3$ or even denser k -point meshes. Furthermore we note that the above argument for the asymptotic behaviour will not hold in the case of metallic systems where orbitals can become degenerate at the Fermi energy and divergences occur.²⁶

An interpolation of $S(\mathbf{G})$ in the range of $0 < |\mathbf{G}| < G_{\min}$ would allow for calculating a finite size correction. In this work, we perform a spherical averaging procedure of $S(\mathbf{G})$ for all radii that are equal to $|\mathbf{G}|$, where \mathbf{G} corresponds to any grid point included in the employed basis set. Note that the spherical averaging of $S(\mathbf{G})$ at a given plane wave vector length is complicated by the fact that the regular plane wave vector grid is only dependent on the cutoff, k -point mesh, and unit cell geometry. Therefore certain directions are oversampled at a given $|\mathbf{G}|$. To get a more accurate estimate of the spherical average of $S(\mathbf{G})$, we proceed as follows. A Fibonacci grid on a sphere is constructed. The values for $S(\mathbf{G})$ at the new grid points are obtained from linear interpolation using the data of the regular grid. Once obtained we can perform a spherical averaging for any given radius $|\mathbf{G}|$. The resultant function $S_{\text{avg}}(|\mathbf{G}|)$ is smooth and isotropic. The inset of Fig. 1 shows the obtained $S_{\text{avg}}(|\mathbf{G}|)$ for the example of a carbon diamond crystal using coupled cluster singles and doubles theory. Once $S_{\text{avg}}(|\mathbf{G}|)$ is obtained, an interpolation of this function around the Coulomb singularity in reciprocal space can be performed. Note that $S_{\text{avg}}(0) = 0$. We use cubic spline interpolation to get an estimate of $S_{\text{avg}}(|\mathbf{G}|)$ for the arbitrary values of $|\mathbf{G}|$ in the range $0 < |\mathbf{G}| < G_{\min}$.

We note that the cubic spline interpolation and the calculated finite size correction strongly depend on the choice for the derivative of S_{avg} at $|\mathbf{G}| = 0$. We investigate three different choices for the derivative of S_{avg} at $|\mathbf{G}| = 0$: (i) the finite size correction referred to as FSN employs the natural boundary condition in cubic spline interpolation, which sets the second derivative of S_{avg} to zero at $|\mathbf{G}| = 0$, (ii) the finite size correction referred to as FSR fixes the derivative to a value calculated from the random-phase approximation plus second-order screened exchange theory (RPA+SOSEX),²⁷ and (iii) the finite size correction FS0 fixes the first derivative of S_{avg} at $|\mathbf{G}| = 0$ to zero as suggested by analytical derivations. We will employ FSR only for the correction of finite size (FS) errors in CCSD theory. Note that the computational cost of CCSD and RPA+SOSEX theory scales as $O(N^6)$ and $O(N^5)$, respectively, where N is a measure for the system size.

The central idea of the proposed finite size correction is to correct the conventional correlation energy expression given in Eq. (2) with an estimate of the correlation energy contribution from the $\mathbf{G} = 0$ volume element. To this end we partition the Coulomb kernel in two parts, labelled short- and long-range, respectively. We choose the kernels such that

$$v(\mathbf{G}) = v^{\text{sr}}(\mathbf{G}) + v^{\text{lr}}(\mathbf{G}), \quad (3)$$

$$v^{\text{sr}}(\mathbf{G}) = \frac{4\pi}{\mathbf{G}^2} (1 - f_{\text{win}}(\mathbf{G})), \quad (4)$$

$$v^{\text{lr}}(\mathbf{G}) = \frac{4\pi}{\mathbf{G}^2} (f_{\text{win}}(\mathbf{G})). \quad (5)$$

The window function switches smoothly between v^{sr} and v^{lr} and is defined as

$$f_{\text{win}}(\mathbf{G}) = \frac{\cos(|\mathbf{G}|/G_c\pi) + 1}{2} \Theta(G_c - |\mathbf{G}|). \quad (6)$$

We will return to the discussion of G_c at the end of this section. The above partitioning allows for splitting the correlation energy contribution in two parts that are given by

$$E_c = E_c^{\text{sr}} + E_c^{\text{lr}}, \quad (7)$$

$$E_c^{\text{lr}} = \sum_{\mathbf{G}}' v^{\text{lr}}(\mathbf{G}) S(\mathbf{G}), \quad (8)$$

$$E_c^{\text{sr}} = \sum_{\mathbf{G}}' v^{\text{sr}}(\mathbf{G}) S(\mathbf{G}). \quad (9)$$

Replacing $S(\mathbf{G})$ with $S_{\text{avg}}(|\mathbf{G}|)$ in Eq. (8) and integrating the long-range contribution directly yield our final expression for the correlation energy including the finite size correction

$$E_c = E_c^{\text{sr}} + \int_{|\mathbf{G}|} M_k \Omega S_{\text{avg}}(|\mathbf{G}|) v^{\text{lr}}(\mathbf{G}) d\mathbf{G}. \quad (10)$$

Ω refers to the unit cell volume. We now return to the discussion of G_c . It seems natural to choose $G_c = G_{\text{min}}$. This implies that we only correct for electronic correlation effects that exceed the length scale of the employed simulation (unit/super) cell. Furthermore this choice also ensures that the finite size correction vanishes in the limit $N_k \rightarrow \infty$.

III. RESULTS

Figure 2 shows the convergences of correlation energy errors with respect to N_k^{-3} , where N_k refers to the number of k -points used to sample the first Brillouin zone in each direction. The errors are calculated with respect to a reference value that has been obtained from a N_k^{-3} extrapolation. The results are shown for the LiH, MgO, BN, and C crystals. The correlation energies have been obtained on the level of second-order Møller-Plesset perturbation theory (MP2), coupled-cluster singles and doubles (CCSD) theory, and the random-phase approximation plus second-order screened exchange (RPA+SOSEX). Without finite size corrections the correlation energies exhibit a $1/N_k^3$ asymptotic behaviour.

Figure 2(a) shows that the FSN correction substantially increases the rate of convergence in MP2 theory. We note that all points that lie within the grey area agree with the thermodynamic limit results obtained from extrapolation to within

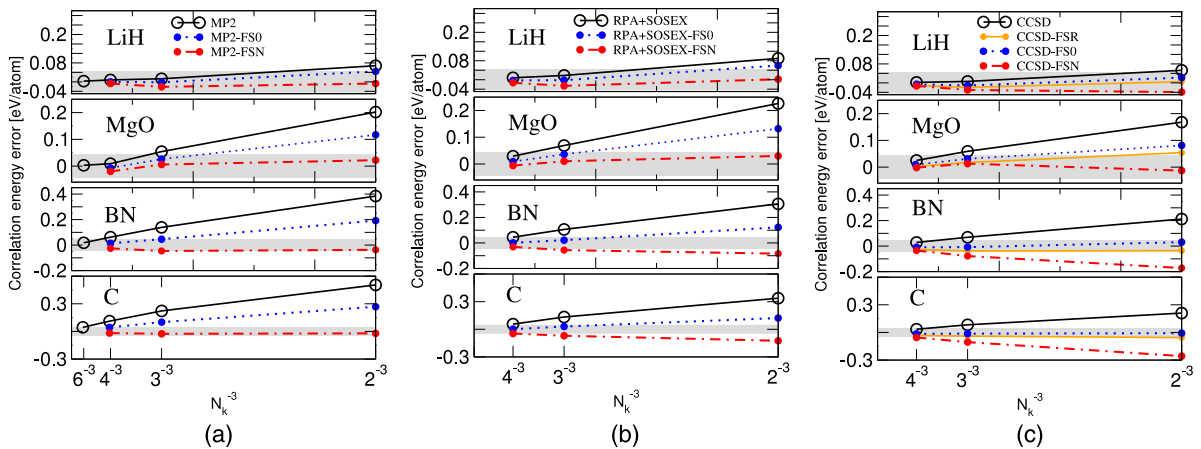


FIG. 2. Convergence of electronic correlation energy finite size errors for LiH, LiF, Si, and C solids obtained using MP2 theory (a), RPA+SOSEX theory (b), and CCSD theory (c). The calculations employed 32 orbitals per k -point. All calculations have been performed using the projector augmented wave method and a plane wave basis set as implemented in the Vienna *ab initio* simulation package (VASP).^{13–15} The sum over plane wave vectors has been restricted to all plane waves with a kinetic energy below 400 eV. The lattice constants have been fixed to experimental equilibrium lattice constants.

chemical accuracy. All MP2-FSN correlation energies are converged to within chemical accuracy (43 meV/atom) using a $2 \times 2 \times 2$ k -point mesh only compared to the thermodynamic limit results. The FS0 correction underestimates the finite size error at small k -point mesh sampling densities. However, both methods improve upon the convergence compared to MP2 theory without finite size corrections.

Figure 2(b) shows that FSN also increases the rate of convergence for RPA+SOSEX theory. However, FSN overestimates the correction for the FS errors and yields results that converge from below with the exception of MgO. Chemical accuracy for all systems is only achieved using $4 \times 4 \times 4$ k -point meshes. On the other hand, FS0 yields underestimated finite size corrections. However, overall both methods yield correlation energies that are significantly closer to the converged results compared to their uncorrect counterparts especially at coarse k -point meshes.

We now turn to the CCSD results depicted in Fig. 2(c). CCSD including FSN overestimates the correction for the finite size error in particular for BN and C. However, since RPA+SOSEX theory is computationally cheaper than CCSD theory, we can perform RPA+SOSEX theory calculations using a $4 \times 4 \times 4$ k -point mesh and the HF reference to get an estimate of the slope of S_{avg} at the corresponding G_{min} . The random-phase approximation is expected to give a very accurate estimate of this slope, which is employed in the finite size correction referred to as FSR. Figure 2(c) shows that CCSD-FSR theory results exhibit a substantially improved rate of convergence compared to CCSD and CCSD-FSN theory. CCSD-FSR energies are converged to within chemical accuracy for all systems using $3 \times 3 \times 3$ k -point meshes only. Furthermore we note that CCSD-FS0 theory achieves a similar accuracy and improvement in convergence rate as CCSD-FSR theory.

IV. CONCLUSION

In summary we have outlined a novel method to correct for finite size errors in the calculation of correlation energies using periodic MP2, RPA+SOSEX, and coupled cluster theories. Chemical accuracy can be achieved in the convergence of CCSD correlation energies using only $3 \times 3 \times 3$ k -point meshes for two atomic unit cells. We

stress that the computational cost of canonical coupled cluster theories scales as M_k^4 . Therefore a twofold reduction of M_k reduces the computational cost by an order of magnitude, greatly simplifying the calculation of solids on the level of CCSD theory. Future work will focus on the application of the proposed finite size correction to metals and the combination with F12 methods.

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