Many-Body Quantum Chemistry for the Electron Gas: Convergent Perturbative Theories

James J. Shepherd[*]

Chemistry Department, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, United Kingdom

Andreas Grüneis[†]

Faculty of Physics and Center for Computational Materials Science, University of Vienna, Sensengasse 8/12, A-1090 Vienna, Austria

We investigate the accuracy of a number of wave function based methods at the heart of quantum chemistry for metallic systems. Using the Hartree-Fock wave function as a reference, perturbative (Møller-Plesset) and coupled cluster theories are used to study the uniform electron gas model. Our findings suggest that nonperturbative coupled cluster theories are acceptable for modeling electronic interactions in metals while perturbative coupled cluster theories are not. Using screened interactions, we propose a simple modification to the widely used coupled cluster singles and doubles plus perturbative triples method that lifts the divergent behavior and is shown to give very accurate correlation energies for the homogeneous electron gas.

Introduction.—The accurate solution of the many-electron Schrödinger equation for real solid-state systems is a major challenge for the field of theoretical condensed matter physics and holds the key to understanding materials with some of the most intriguing and commercially valuable properties, such as high T_c cuprates and transition metal oxides. Moreover, it provides access to properties of materials under conditions that are not accessible by experiment. In recent years, a number of authors using quantum chemical methods such as second-order Møller-Plesset (MP2) and coupled cluster singles and doubles (CCSD) theory have made significant progress towards finding accurate solutions for real materials [1–12]. Thanks to recent methodological advances and the increase in available computer power, these methods have become tractable for simple materials despite their computational cost. It has been shown that coupled cluster theory, one of the most accurate and widely used quantum chemical methods, translates its high accuracy and systematic improvability seamlessly from molecular systems to semiconductors and insulators, including even more strongly correlated systems such as NiO [1].

The development of these and other highly accurate as well as predictive *ab initio* methods is also partly motivated by their potential use for studying metal-insulator transitions in transition metals oxides, where currently available density functionals fail [13]. However, so far very little is known about the accuracy of quantum chemical wave function based methods for metallic systems. An open question of growing importance surrounding this field is to directly address which methods are appropriate and which are not for the study of metallic systems. Approximations and divergences need to be understood so that needless effort is not expended investigating methods which will ultimately fail. Although it would in

principle be possible to pursue this question with analytical theory, the plurality of diagrams and the lack of closed solutions makes this attempt intractable. To this end, we aim to provide here a simple, novel, and robust methodology to test for the numerical convergence of approximate methods in metals using the finite basis set simulation-cell electron gas [14–16]. Furthermore, we propose modifications to the employed quantum chemical methods that account for screening effects and correct deficiencies of perturbative Møller-Plesset and coupled cluster theories in metals.

Theory.—In this work we will employ various quantum chemical methods that use Hartree-Fock (HF) theory as a reference and treat electronic correlation by expanding the many-electron wave function in a multideterminantal basis. The electronic correlation energy in MP2 and CCSD theory is nonvariational and for the systems studied in this work can be calculated by

$$E^c = \frac{1}{4} \sum_{i,j} \sum_{a,b} t_{ij}^{ab} \langle \Psi_{\mathrm{HF}} | H | \Psi_{ij}^{ab} \rangle. \qquad (1)$$

The indices i, j, k, l and a, b, c, d will be used throughout this work to refer to occupied and unoccupied HF spin orbitals, respectively. In the above expression, Ψ_{ij}^{ab} are HF Slater determinants where the occupied orbitals i and j have been replaced with virtual orbitals a and b. The t_{ij}^{ab}'s refer to the coefficients of the doubly excited Slater determinants and their definition for the various wave function based methods will be given later. We note that the singly excited Slater determinants make no contribution to the wave functions and correlation energies of the systems studied in the present Letter.

In this work, we seek to investigate the accuracy of various wave function based methods for an archetypal

fully three-dimensional metallic system. The homogeneous electron gas [(HEG), uniform electron gas, or jellium model] is well regarded to be the simplest model for a metallic system consisting of N electrons in a box of length L with a two-electron Ewald interaction $\hat{v}_{\alpha\beta}$ [17,18],

$$\hat{H} = \sum_{\alpha} -\frac{1}{2}\nabla_{\alpha}^2 + \sum_{\alpha\neq\beta}\frac{1}{2}\hat{v}_{\alpha\beta} + \text{const.} \quad (2)$$

In the thermodynamic limit (TDL), found as the particle number tends to infinity ($N \rightarrow \infty$) with the density held constant, it is possible to solve the above Hamiltonian in the Hartree-Fock approximation using single plane-wave spin orbitals. This yields an analytic expression for the dispersion relation, producing a band structure with a zero in the density of states at the Fermi energy [19]; this complicates analytical derivations.

In setting out to find the behavior of approximate theories to obtain the correlation energy (i.e., the total energy with Hartree-Fock energy as a starting point), it is typical to begin with a finite simulation-cell model of N electrons, and carefully approach the thermodynamic limit by extrapolation [18,20]. However, in quantum chemical techniques, we must also make do with a finite one-particle basis set. The difficulty of investigating the properties of these approximate theories in the thermodynamic limit is hampered by this requirement of a finite basis set, in this case M plane-wave spin orbitals defined by a kinetic energy cutoff $1/2k_c^2$. In principle, the complete basis set limit $k_c \rightarrow \infty$ and thermodynamic limit $N \rightarrow \infty$ must be found, which is prohibitively costly given the scaling of even approximate quantum chemical theories.

The most obvious way to make progress towards these limits is to take the $k_c \rightarrow \infty$ limit, to solve the N-electron Hamiltonian at the complete basis set limit, and then the $N \rightarrow \infty$ limit can be found latterly. However, in this Letter we propose to take the $N \rightarrow \infty$ limit first for a finite $k_c = \gamma k_F$ [21]. Figure 1 illustrates this approach schematically for a two-dimensional reciprocal lattice. As the $N \rightarrow \infty$ limit is taken, the band gap closes because the grid spacing in the region around the Fermi surface becomes smaller, and the zero-momentum excitations that cause the
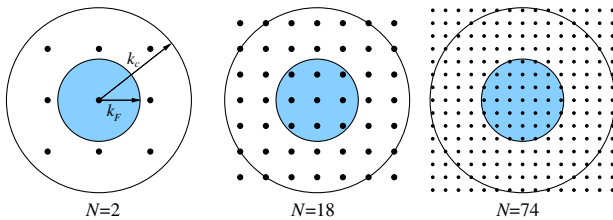

FIG. 1 (color online). Schematic illustration of two-dimensional reciprocal lattice for different electron numbers N ($N = 2$, 18, and 74) and a fixed density. k_F and k_c denote the length of the Fermi and basis set cutoff wave vector, respectively. The length of these wave vectors is constant for a fixed density.

divergences in, for example, MP2 theory are increasingly well represented in a size-extensive fashion.

Results.—We first outline how to show the well-known divergence in the MP2 energy (e.g. Ref. [22]) using finite-M, finite-N calculations and then generalize this approach to demonstrate limiting behaviors in other theories. The amplitudes in MP2 theory are given by

$$t_{ij}^{ab} = \frac{\langle\Psi_{ij}^{ab}|\hat{v}|\Psi^{\text{HF}}\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (3)$$

where ϵ are the Hartree-Fock eigenvalues of the spin orbitals and they are employed for the evaluation of the MP2 correlation energy according to Eq. (1).

MP2 correlation energies per electron are presented in Fig. 2 for sets of finite-N electron gases. As the electron number increases, the HF gap becomes smaller. Concomitantly, the MP2 correlation energy per electron increases linearly with the decreasing HF gap. This conclusively demonstrates that our approach recovers the expected divergence and physical behavior from this method. We stress that any approximate method suitable for metals and solids in general is required to yield correlation energies per electron that converge to a constant in the $N \rightarrow \infty$ limit. To further validate this as an approach accurately capturing the TDL, we compare this with the finite-basis electron gas energies from identically constructed random-phase approximation (RPA) calculations, which show a convergent behavior (with a finite-size error as $\sim N^{-1}$ [20]) as anticipated. All RPA results in this work are calculated using a HF reference. We note that the RPA referred to in this work corresponds to the so-called direct RPA in which the employed two-electron integrals are not antisymmetrized.

We now return to the divergence of the MP2 correlation energy and show that it can be lifted by replacing the bare Ewald interaction with a screened interaction in Eq. (3). In this approach, the "screened MP2" amplitudes are given by

$$t_{ij}^{ab} = \frac{\langle\Psi_{ij}^{ab}|\hat{v}_{\text{TF}}|\Psi^{\text{HF}}\rangle}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}, \quad (4)$$

where $\hat{v}_{\text{TF}}$ refers to the Thomas-Fermi screened Coulomb interaction. These amplitudes yield correlation energies per electron that converge for metallic systems with a rate similar to RPA, as shown in Fig. 2. However, the screened MP2 energies strongly underestimate the true correlation energy.

We note that the introduction of the Thomas-Fermi screening is difficult to motivate in Møller-Plesset perturbation theory. In Hedin's GW theory, however, this corresponds to a static approximation of the frequency-dependent screened electron interaction W calculated in the RPA [23]. As such, our choice of screening has two advantages: (i) for homogeneous systems, the screening length depends on the electronic density only and the
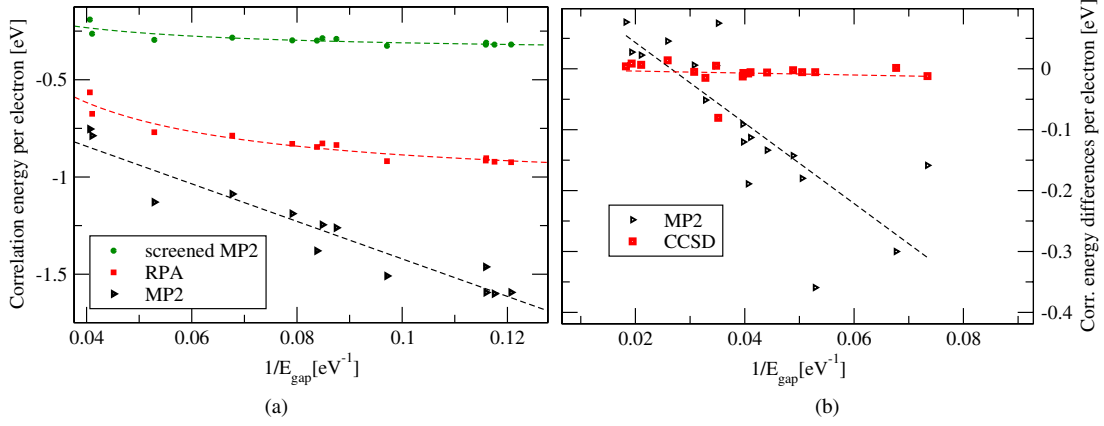
FIG. 2 (color online).   (a) Screened MP2, unscreened MP2, and RPA energies for a variety of finite-basis simulation-cell electron gases with electron numbers $N = 14$–730 corresponding to closed-shell configurations of a simple cubic reciprocal-space lattice. (b) Differences between the RPA and MP2/CCSD correlation energies ($r_s = 1.0$ a.u., $\gamma = \sqrt{2}$) show that MP2 is divergent as the band gap closes (on approach to the thermodynamic limit). CCSD is convergent to a constant energy offset with respect to RPA which is only serendipitously close to zero for this r_s and γ. (This agreement is the crossover between CCSD and RPA due to overcorrelation on approach to the complete basis set limit similar to that seen in Fig. 5(b) in Ref. [16].)

screened interaction is readily given by $v_{\text{TF}}(r) = e^{-k_0 r}/r$, where k_0 is the Thomas-Fermi wave vector, and (ii) in the case of inhomogeneous systems, one can employ the W calculated in the RPA of already existing GW implementations.

Having now numerically demonstrated the well-accepted behavior for the MP2 energy, we turn our attention towards another approximate and widely used quantum chemical method for which the behavior on approach to the TDL is unverified—CCSD. The CCSD doubles amplitudes are obtained by solving the so-called amplitude equations given by $\langle \Psi_{ij}^{ab} | e^{-T} H e^T | \Psi^{\text{HF}} \rangle = 0$, where $T = T_2 = (2!)^{-2} \sum_{ij} \sum_{ab} t_{ij}^{ab} \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_j \hat{c}_i$ for the HEG [24,25]. We note in passing that CCSD and coupled cluster doubles theory (CCD) are equivalent for the homogeneous electron gas due to the complete absence of symmetry-allowed single excitations in its many-body expansion. $\hat{c}_n^\dagger$ ($\hat{c}_n$) are electron creation (annihilation) operators.

There has been surprisingly little literature concerning coupled cluster theory for solids, in spite of the wealth of applications they have received in the molecular quantum chemistry community. This is also true for the homogeneous electron gas, and although there has been some discussion of CCSD with approximate amplitude equations, these more closely resemble the RPA equations [26–29]. As such, to the best of our knowledge, the question of whether CCSD diverges in the TDL for metallic systems has not yet been conclusively addressed.

Because of the relatively expensive scaling of such methods, simulations of an $N = 730$ electron gas with current fully periodic codes [30] are prohibitively expensive. However, we have found that further reduction in finite-size effects can be achieved by taking the difference between the CCSD energy with the RPA energy, and in this

difference the limiting behavior is more clear due to cancellations in the N^{-1} term. We have also taken advantage of other simulation-cell lattices (face-centered cubic and body-centered cubic) to provide more closed-shell configurations. Taking energy differences in this way allows us to clearly demonstrate in Fig. 2 that the CCSD energy converges at the same rate as RPA [31]. Even though CCSD is exact through third-order perturbation theory, it performs a resummation of infinitely many contributions to the correlation energy (for instance all bubble diagrams as in RPA) of higher-order terms that lift the divergence of order-by-order perturbation theory for metals. Furthermore, CCSD includes ladder diagrams that are understood to be important in the description of correlation at low densities [32].

Having demonstrated the convergent behavior for the CCSD energy, we now turn our attention to the perturbative triples (T) correction to CCSD [25,33]. CCSD(T) theory employs an exponential ansatz for the wave function given by $e^T \Psi_{\text{HF}}$, where $T = T_1 + T_2 + T_3$ and $T_3 = (3!)^{-2} \sum_{ijk} \sum_{abc} t_{ijk}^{abc} \hat{c}_a^\dagger \hat{c}_b^\dagger \hat{c}_c^\dagger \hat{c}_k \hat{c}_j \hat{c}_i$. The corresponding triples amplitudes t_{ijk}^{abc} are calculated in a perturbative way reading

$$t_{ijk}^{abc} = \frac{\langle \Psi_{ijk}^{abc} | [\hat{v}, T_2] | \Psi^{\text{HF}} \rangle}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}. \quad (5)$$

Once obtained, the coupling of the triples with the doubles amplitudes is considered only in an approximate fashion and its contribution to the CCSD correlation energy is calculated by

$$E^{(\text{T})} = \sum_{ij} \sum_{ab} t_{ij}^{ab} \langle \Psi_{ij}^{ab} | [H, T_3] | \Psi^{\text{HF}} \rangle, \quad (6)$$
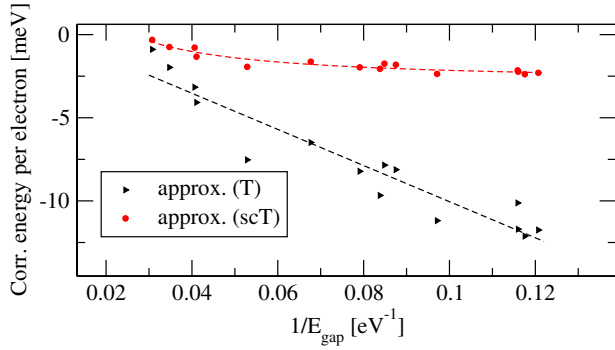
FIG. 3 (color online). Approximate screened and unscreened perturbative triples correlation energies per electron for a range of finite-electron number calculations using $r_s = 1.0$ a.u. and $\gamma = \sqrt{2}$.
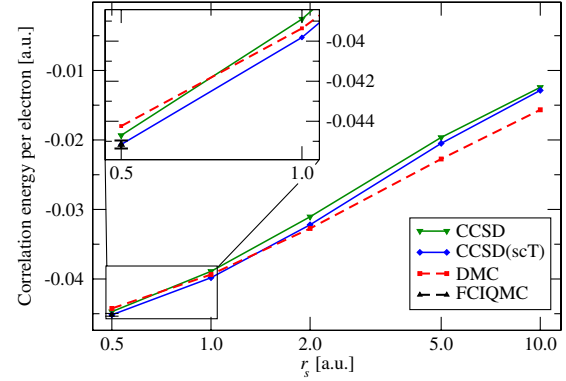

FIG. 4 (color online). Complete basis set limit correlation energies per electron of DMC, CCSD, CCSD(scT), and FCIQMC for a range of densities. The exact FCIQMC and DMC SJ3 backflow results are taken from Ref. [14] and Ref. [38], respectively.

where the t_{ij}^{ab} amplitudes are obtained from an underlying CCSD calculation.

Exploring the behavior of Eq. (6) for large electron numbers ($N > 200$) is hindered by the large computational cost. As such, we seek to investigate the behavior of $E^{(T)}$ for metals by approximating Eq. (6) in a manner that leaves the qualitative behavior unchanged. We therefore approximate the CCSD amplitudes t_{ij}^{ab} in the above expression by screened MP2 amplitudes from Eq. (4). We have shown before that these amplitudes lead to a convergence of the MP2 energy at the same rate as the CCSD and RPA energy. Figure 3 shows that the approximate (T) energy expression from Eq. (6), however, clearly diverges for metals at the same rate as MP2. From this we conclude that the full (T) contribution to the CCSD(T) correlation energy diverges as well and that CCSD(T) is not a suitable method for metals.

We can now apply the same modification to the expression for the perturbative triples amplitudes in Eq. (5) as we have done for the screened MP2 amplitudes. Replacing $\hat{v}$ in Eq. (5) with $\hat{v}_{\mathrm{TF}}$ yields

$$t_{ijk}^{abc} = \frac{\langle \Psi_{ijk}^{abc} | [\hat{v}_{\mathrm{TF}}, T_2] | \Psi^{\mathrm{HF}} \rangle}{\epsilon_i + \epsilon_j + \epsilon_k - \epsilon_a - \epsilon_b - \epsilon_c}. \quad (7)$$

Figure 3 demonstrates that the energies per electron calculated in the manner described above converges for $N \to \infty$. From this we conclude that the divergence for metallic systems of the full perturbative triples correction can be lifted by using a screened interaction kernel for the evaluation of triples amplitudes.

To test the accuracy of CCSD and CCSD(scT) (CCSD and screened perturbative triples), we calculate the complete basis set limit correlation energies for the 54 electron system and compare to diffusion Monte Carlo (DMC) and full configuration interaction quantum Monte Carlo (FCIQMC) results for a range of realistic metallic densities. The basis set extrapolations on the level of the wave function based methods were carried out using $M = 700$–1600 plane waves and the procedures outlined in

Ref. [16]. Figure 4 shows the correlation energies of the different methods. Our findings show that CCSD and CCSD(scT) become more accurate as the electronic density increases. For very high densities ($r_s = 0.5$ a.u.) the quantum chemical wave function based methods yield energies below those of DMC. Although coupled cluster methods are nonvariational, the comparison to exact FCIQMC results shows that CCSD and CCSD(scT) are closer to the exact energies in this density regime. As the electronic density decreases, the coupled cluster methods capture less correlation energy. We attribute this tendency to the increasing multireference character of the HEG wave function at lower densities, which is difficult to treat with coupled cluster methods. This is likely affected by the presence of a phase transition to the Wigner crystal, which, however, occurs at much lower densities than studied here [34].

Concluding remarks.—In summary, we have shown that a judicious choice of finite-size and finite-electron number homogeneous electron gas models can be used to demonstrate the limiting behavior of the correlation energy in approximate many-body theories for metallic systems with modest computational cost. By comparing to RPA correlation energies, we have controlled for basis set incompleteness and finite-size errors. As a first application of the outlined methodology, we have verified the divergence of MP2 energies in metals. Furthermore, we have shown that CCSD converges for metals at the same rate as RPA with respect to the system size N. We have shown that the divergence in MP2 can be lifted by using a Thomas-Fermi screening in the calculation of MP2 amplitudes and yields a rate of convergence that is similar to the RPA and CCSD theory. The screened MP2 approximation captured, however, only about half of the CCSD correlation energy in the same basis set.

The divergence of CCSD(T) for metals has been investigated by approximating the CCSD amplitudes with screened MP2 amplitudes. We have found that

approximate (T) correlation energies per electron diverge as $N \rightarrow \infty$ and concluded from this observation that the CCSD(T) method is not suitable for treating electron correlations in metals. However, by the introduction of the Thomas-Fermi screening in the calculation of the triples amplitudes, this divergence can be lifted. We demonstrated that the electronic correlation energies for the 54-electron system obtained using CCSD(scT) were in good agreement with DMC results despite showing a tendency to capture less correlation for lower densities. Going beyond the electron gas, it should be possible to model the screening with preexisting *ab initio GW* codes (e.g., Ref. [30]).

In the high-density regime ($r_s \leq 1.5$ a.u.) of the electron gas, CCSD(scT) recovered the correlation energy to high accuracy. Even though it is well understood that in the high-density limit the RPA plus a correction from second-order exchange yields highly accurate results for the electron gas [26,35], the accuracy of these methods is not transferable to real systems [36,37]. This is in contrast to CC methods that are amongst the only wave function based methods that routinely achieve chemical accuracy with polynomially scaling computational cost [25]. It is hoped that the developments presented here will be of interest to the growing field aiming to study condensed matter systems with these techniques.

---

*js615@cam.ac.uk

†andreas.grueneis@univie.ac.at

[1] G. H. Booth, A. Grüneis, G. Kresse, and A. Alavi, Nature (London) **493,** 365 (2012).

[2] M. D. Ben, J. Hutter, and J. VandeVondele, J. Chem. Theory Comput. **8,** 4177 (2012).

[3] C. Müller and B. Paulus, Phys. Chem. Chem. Phys. **14,** 7605 (2012).

[4] L. Maschio, D. Usvyat, F. R. Manby, S. Casassa, C. Pisani, and M. Schütz, Phys. Rev. B **76,** 075101 (2007).

[5] S. Casassa, M. Halo, L. Maschio, C. Roetti, and C. Pisani, Theor. Chem. Acc. **117,** 781 (2007).

[6] P. Ayala, K. Kudin, and G. Scuseria, J. Chem. Phys. **115,** 9698 (2001).

[7] D. Usvyat, B. Civalleri, L. Maschio, R. Dovesi, C. Pisani, and M. Schütz, J. Chem. Phys. **134,** 214105 (2011).

[8] M. Marsman, A. Grüneis, J. Paier, and G. Kresse, J. Chem. Phys. **130,** 184103 (2009).

[9] H. Stoll and K. Doll, J. Chem. Phys. **136,** 074106 (2012).

[10] S. J. Nolan, M. J. Gillan, D. Alfè, N. L. Allan, and F. R. Manby, Phys. Rev. B **80,** 165109 (2009).

[11] S. J. Binnie, S. J. Nolan, N. D. Drummond, D. Alfè, N. L. Allan, F. R. Manby, and M. J. Gillan, Phys. Rev. B **82,** 165431 (2010).

[12] P. Schwerdtfeger, B. Assadollahzadeh, and A. Hermann, Phys. Rev. B **82,** 205111 (2010).

[13] M. Marsman, J. Paier, A. Stroppa, and G. Kresse, J. Phys. Condens. Matter **20,** 064201 (2008).

[14] J. J. Shepherd, G. Booth, A. Grüneis, and A. Alavi, Phys. Rev. B **85,** 081103 (2012).

[15] J. J. Shepherd, G. H. Booth, and A. Alavi, J. Chem. Phys. **136,** 244101 (2012).

[16] J. J. Shepherd, A. Grüneis, G. H. Booth, G. Kresse, and A. Alavi, Phys. Rev. B **86,** 035111 (2012).

[17] P. Ewald, Ann. Phys. (Leipzig) **64,** 253 (1921).

[18] L. M. Fraser, W. M. C. Foulkes, G. Rajagopal, R. J. Needs, S. D. Kenny, and A. J. Williamson, Phys. Rev. B **53,** 1814 (1996).

[19] R. Martin, *Electronic Structure* (Cambridge University Press, Cambridge, England, 2004).

[20] N. D. Drummond, R. J. Needs, A. Sorouri, and W. M. C. Foulkes, Phys. Rev. B **78,** 125106 (2008).

[21] Taking a finite-basis approach to the homogeneous electron gas has only recently been introduced to the literature [14–16].

[22] A. Grüneis, M. Marsman, and G. Kresse, J. Chem. Phys. **133,** 074107 (2010).

[23] L. Hedin, Phys. Rev. **139,** A796 (1965).

[24] S. Hirata, R. Podeszwa, M. Tobita, and R. J. Bartlett, J. Chem. Phys. **120,** 2581 (2004).

[25] R. J. Bartlett and M. Musial, Rev. Mod. Phys. **79,** 291 (2007).

[26] D. L. Freeman, Phys. Rev. B **15,** 5512 (1977).

[27] R. F. Bishop and K. H. Lührmann, Phys. Rev. B **17,** 3757 (1978).

[28] R. F. Bishop and K. H. Lührmann, Phys. Rev. B **26,** 5523 (1982).

[29] S. Hirata and Y. Ohnishi, Phys. Chem. Chem. Phys. **14,** 7800 (2012).

[30] http://www.vasp.at.

[31] The outliers at ~ 0.035 and ~ 0.075 eV^{-1} are due to these (bcc) systems having spuriously low and high band gaps, respectively, due to the lattice shape.

[32] R. D. Mattuck, *A Guide to Feynman Diagrams in the Many-Body Problem* (Dover, New York, 1967).

[33] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157,** 479 (1989).

[34] N. D. Drummond, Z. Radnai, J. R. Trail, M. D. Towler, and R. J. Needs, Phys. Rev. B **69,** 085116 (2004).

[35] P. Nozières and D. Pines, Phys. Rev. **111,** 442 (1958).

[36] A. Grüneis, M. Marsman, J. Harl, L. Schimka, and G. Kresse, J. Chem. Phys. **131,** 154115 (2009).

[37] J. Paier, X. Ren, P. Rinke, G. E. Scuseria, A. Grüneis, G. Kresse, and M. Scheffler, New J. Phys. **14,** 043002 (2012).

[38] P. Lopez Ríos, A. Ma, N. D. Drummond, M. D. Towler, and R. J. Needs, Phys. Rev. E **74,** 066701 (2006).