Self-Consistent Calculation of Total Energies of the Electron Gas Using Many-Body Perturbation Theory

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Abstract

The performance of many-body perturbation theory for calculating ground-state properties is investigated. We present fully numerical results for the electron gas in three and two dimensions in the framework of the *GW* approximation. The overall agreement with very accurate Monte Carlo data is excellent, even for those ranges of densities for which the *GW* approach is often supposed to be unsuitable. The latter seems to be due to the fulfilment of general conservation rules. These results open further prospects for accurate calculations of ground-state properties circumventing the limitations of standard density functional theory.

71.10.-w, 71.10.Ca, 05.30Fk

I. INTRODUCTION

Many-body perturbation theory (MBPT), particularly in Hedin's *GW* approximation[1], has been used extensively to calculate quasiparticle (QP) energies and spectra of a wide variety of electron systems[2]. The *GW* method offers a simple way to determine the one-electron Green's function, $\widehat{G}$, from which the QP properties can be easily extracted. However, $\widehat{G}$ also contains information about ground-state properties: the expectation value of any one-particle operator can be expressed in terms of $\widehat{G}$, and by using the Galitskii-Migdal formula[3] the total energy may also be obtained. Nonetheless, the capability of a Green's function MBPT to provide reliable ground-state energies has not been fully explored so far. The few available results are restricted to the spin-unpolarized homogeneous electron gas (HEG) in the range of metallic densities (i.e., $r_{\rm s} = 2 \sim 5$ a.u.)[4–6]. These investigations suggest that the *GW* approach could produce accurate electron total energies, but a deeper study is needed to provide an overall assessment of this issue. This is an important question because many of the limitations of the usual implementations of density functional theory (DFT)[7], can be circumvented by using MBPT total-energy calculations. Indeed, well-recognized failures of the DFT in its usual approximations (for instance when studying van der Waals forces[8], chemical reactions[9], defects in semiconductors[10], or quasi-two dimensional systems[11]) are mainly due to the limited account of non-local effects that, on the contrary, are included in the *GW* approximation. On the other hand, quantum Monte Carlo (QMC) methods are being applied to more and more systems[12], but they require a large computational effort. In this context, MBPT has to be regarded as a good candidate to supersede standard DFT schemes [like the local density (LDA) and the generalized gradient approximations] without implying a prohibitive computational task. To provide insights into the above points, in this Paper we present *GW* results for the ground-state properties of the three-dimensional HEG (covering a broad range of densities in both spin-unpolarized and fully spin-polarized phases) and of the two-dimensional HEG. To do so we have used the *space-time* numerical procedure developed by Rojas *et al.*[13]. This method permits efficient and stable computa-

tion of the full self-energy operator $\widehat{\Sigma}$ and the corresponding Green's function $\widehat{G}$[14], with the precision needed for a converged evaluation of the total energy.

II. THEORY

In MBPT, the Green's function and the self-energy of a system of N electrons under a external potential $v_{\text{ext}}(\mathbf{r})$ are linked through the Dyson equation

$$\widehat{G}^{-1}(\omega) = \widehat{G}_0^{-1}(\omega) - \left[\widehat{\Sigma}(\omega) + (\Delta v - \Delta\mu)\,\widehat{1}\right] , \tag{1}$$

where the usual matrix operations are implied. $\widehat{G}_0(\omega)$ is the Green's function of a fictitious system of N non-interacting electrons under the potential $v_0(\mathbf{r})+\Delta\mu$, $\Delta v = v_{\text{H}}+v_{\text{ext}}-v_0$ (v_{H} being the exact Hartree potential), and $\Delta\mu$ is a constant that aligns the chemical potential of the fictitious system with the actual one, μ.[15]. In the GW framework, $\widehat{\Sigma}$ is approximated by

$$\Sigma(1,2) = i\,G\left(1,2^{+}\right) W(1,2) , \tag{2}$$

where the labels 1,2 symbolize space-time coordinates. $\widehat{W}$ is the screened Coulomb potential which is related to the bare Coulomb interaction w and the polarizability $\widehat{P}$ by

$$\widehat{W}(\omega) = \widehat{w} + \widehat{w}\,\widehat{P}(\omega)\,\widehat{W}(\omega) . \tag{3}$$

Finally, under the GW approach we have[16]

$$\widehat{P}(1,2) = -2i\,G(1,2)\,G\left(2,1^{+}\right) . \tag{4}$$

Eq. 1-4 may be solved iteratively to self-consistency. We note that the choice of the fictitious non-interacting system in (1) is arbitrary because the differences arising from different $\widehat{G}_0$s are cancelled out by the terms Δv and $\Delta\mu$. Also, by including the shift $\Delta\mu$ we guarantee that at any step of the iteration, $\widehat{G}$ verifies several exact properties that have to be verified by any realistic Green's function[17], ensuring a smooth and stable convergence of the iterative process. Furthermore, the Hartree potential has to be updated after each iteration, and

this is done by calculating the electron density $n(\mathbf{r})$ from $\widehat{G}$. To evaluate $\Delta\mu$ we need to obtain the chemical potential that is, by definition, the energy of the highest occupied QP energy, calculated at each iteration in terms of the self-energy by solving the QP Schrödinger equation.

The above set of equations defines a *conserving approximation* in the Baym-Kadanoff sense[18]. One consequence is that the total number of particles given by the self-consistent GW Green's function does not change when an external perturbation acts on the system. Besides, it gives the right number of particles for the HEG[19]. The correctness of the number of particles for an arbitrary inhomogeneous system can thus be inferred by regarding the system as the result of an adiabatic transform of the HEG. Another characteristic of a conserving approximation is the absence of ambiguities among different expressions for calculating the total energy. This suggests that a MBPT evaluation of ground-state properties should employ a conserving approximation such as self-consistent GW.

However, routine GW calculations are mainly concerned with the QP properties of real materials and do not attempt self-consistency. Indeed, self-consistency implies a worsening in the description of the QP spectrum rather than an improvement[6,20,21]. Hence, the usual non self-consistent (and non-conserving) GW approach (that we shall denoted as G_0W_0, whereas GW will stand for the fully self-consistent solution of Hedin's equations) is clearly preferred in a spectral context. This failing of GW can be understood in terms of the spectral properties of $\widehat{G}$, but our present interest is very different: issues as those described in the previous paragraph are by far more important than the concrete shape of $\widehat{G}$. Of course these two aspects are not independent, but the development and application of a conserving theory giving at the same time an accurate description of QP spectra is an unsolved formidable challenge.

In G_0W_0, the self-energy is approximated by Eq. 2 supposing that $\widehat{G} = \widehat{G}_0$, whereas the screened Coulomb potential was obtained from (4) and (3) once (i.e., $\widehat{W}$ has been calculated in a RPA fashion). Eventually, the Dyson equation is solved taking into account

that $\Delta v \simeq v_{\mathrm{LDA}}$, where v_{LDA} is the LDA exchange-correlation (XC) potential. Although the term $\Delta\mu$ is often neglected at this stage, in this Paper we will keep this contribution for the reasons explained above. Partial self-consistency (denoted as GW_0) may be achieved by keeping the screened Coulomb potential $\widehat{W}_0$ obtained from a G_0W_0 procedure and, hence, by solving only (1) and (2) iteratively[5,20]. Although the GW_0 is not a conserving approximation, it gives the right number of particles for the HEG (so meeting an important physical point of the GW scheme)[6]. On the other hand, its description of QP properties seems to be only marginally worse than G_0W_0[20]. Finally, there are many other schemes for implementation of the GW equations, but essentially they are focused on the choice of $\widehat{G}_0$ for non self-consistent calculations, and so are meaningless in an homogeneous system.

As mentioned above, we will apply the space-time method[13] to solve the GW equations. Each one is written in the most favorable spatial representation (reciprocal or real), going from one to other using Fourier transforms. However the most important issue is the evaluation of the dynamical dependence on imaginary time or frequency domain. To calculate ground-state properties, a contour deformation avoids the need to obtain $\widehat{G}$ for real frequencies. Concretely, the expectation value of any one-particle operator $\widehat{b}$ is given by

$$\left\langle \widehat{b} \right\rangle = \frac{2}{\pi} \mathrm{Im} \int_C d\omega \, \mathrm{Tr} \left[\widehat{b} \widehat{G} \left(\omega \right) \right], \tag{5}$$

where the frequency is measured from the chemical potential μ, and C is the integral path in the complex frequency plane equal to the circular arc γ from $\omega = -\infty$ to $\omega = -i\infty$ together with the negative imaginary axis. In the same notation, the Galitskii-Migdal formula for the total energy reads

$$E = \frac{1}{\pi} \mathrm{Im} \int_C d\omega \, \mathrm{Tr} \left[\left(\omega + \widehat{h}_0 \right) \widehat{G} \left(\omega \right) \right], \tag{6}$$

$\widehat{h}_0$ being the one-electron hamiltonian with potential $v = v_{\mathrm{ext}} - \mu$. To deal with the evaluation of (5) and (6) we write the Green's function as $\widehat{G} = \widehat{G}_{\mathrm{X}} + \delta\widehat{G}$, $\widehat{G}_{\mathrm{X}}$ being the solution of the Dyson's equation (1), but substituting the full self-energy $\widehat{\Sigma}\left(\omega\right)$ by its frequency-independent part $\Sigma_{\mathrm{X}}\left(1,2\right) = iG\left(1,2^{+}\right) w\left(1,2\right)$. Hence, the frequency integrals can be split up in two

parts. The contribution due to $\widehat{G}_{\rm X}$ is evaluated analytically, whereas for the remainder the only non-zero contribution arises from the imaginary axis, which is amenable for numerical calculation. We have used Gauss-Legendre (GL) grids for imaginary times and frequencies, and the contributions due to points outside the GL grids are treated in an analytical fashion in accordance with the overall numerical procedure given in Ref.[14]. Usually, GL grids with 128 points suffice for well-converged results (better than 1 mHa). For the HEG, matrix inversions are not needed, and a fully self-consistent resolution of the *GW* equations only takes typically a few seconds on a standard workstation.

III. RESULTS AND DISCUSSION

Using different *GW* schemes, we have obtained the XC energy per particle, $\varepsilon_{\rm XC}$ (defined as the difference between the energies of the interacting and non-interacting systems) for the spin-unpolarized ($\zeta = 0$) HEG (Table I and Fig. 1). We first compare our numerical results with the two of von Barth and Holm[6]. A small discrepancy ($1 \sim 2$ mHa) appears, but it is consistent with the error bar (about 3%) of the semi-analytical procedure carried out by these authors[22]. Focusing on the accuracy of the MBPT procedure, we can see that the agreement between the essentially exact diffusion Monte Carlo (QMC)[23,24] and the self-consistent *GW* is almost perfect in the limit of high densities. This is not a surprise because the exchange is treated exactly by the *GW* and it is dominant in this range of densities. However, the quality of the *GW* energies is striking for intermediate and low densities, where the many-body effects not included in the *GW* framework might be expected to be evident. Partial self-consistency (GW_0) yields slightly inferior results, though the differences are no more than a few mHa. The worst results (but, in any case, with errors no greater than 10 mHa for metallic densities) are provided by the non-self-consistent G_0W_0 procedure. G_0W_0 underestimates the total energy, and by achieving partial self-consistency, the spectral weight in the Green's function is blue-shifted, so increasing the total energy. After full self-consistency, such shift is slightly larger, but the kinetic energy is smaller than in GW_0. The

presence of these two opposite trends explains the small differences between GW and GW_0. We have also included (for comparison) the corresponding RPA values[25]. Note that the RPA dielectric function is the same than the G_0W_0 one, and the huge discrepancies between them arise from the different ways in which the evaluation of the total energy is performed.

All the above trends also apply for the fully spin-polarized ($\zeta = 1$) HEG (see Fig. 2), but in this case the errors in the GW energies are marginally greater. (Although not at all the objective of this Paper, it is interesting to note that using the self-consistent GW, the paramagnetic phase is more stable than the ferromagnetic one up to $r_s = 15 \sim 20$, in fair agreement with the QMC value[24] of $r_s = 25 \sim 30$, despite the low density of the system).

Our results for the two-dimensional (2D) HEG are also shown. In 2D systems, correlation effects are much more important; in other words, the diagrams that are neglected in the GW scheme play a relevant role in these low-dimensional problems. As a consequence we cannot expect here extremely accurate results using the GW approximation. However, as we can see in Fig. 3, the GW gives energies near the QMC values[26], resolving partially the inaccuracy of the G_0W_0 approach and greatly improving the RPA energies. We note that in the limit of low densities, GW_0 fits the QMC results slightly better than GW.

Finally, it is now very well known that G_0W_0 does not give the right number of particles for an inhomogeneous system[17,27]. However there were certain doubts whether it recovers the right density of the HEG or not. The use of the space-time method allows us to affirm that G_0W_0 does not give exactly the number of particles also in the homogeneous limit. Whereas the exact density and the G_0W_0 one are indistinguishable up to $r_s = 4$, for $r_s = 5$ the G_0W_0 overestimates the density by 0.3%. The deviation increases when going into the low density region, being 1.7% for $r_s = 10$, and 6.1% for $r_s = 20$.

In summary, we have studied the performance of the GW approximation for the evaluation of ground-state properties. The accuracy of the results is correlated with the fulfillment of conservation rules (that can be achieved by using a self-consistent GW scheme), and the approximations inherent in the GW scheme have much less importance than when calculating QP properties. The dynamical dependences in the GW equations are easy to handle

using a representation in imaginary time and frequency, that may be straightforwardly generalized to arbitrary inhomogeneous systems. Hence, the results presented here can be the point of departure for future accurate evaluations of ground-state properties of electron systems without the limitations of DFT and the complexity of QMC.

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REFERENCES

[1] L. Hedin, Phys. Rev. **139**, A796 (1965); L. Hedin and S. Lundqvist, in *Solid State Physics 23*, ed. by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969).

[2] e.g.: M.S. Hybertsen and S.G. Louie, Phys. Rev. Lett. **55**, 1418 (1985); R.W. Godby, M. Schlüter, and L.J. Sham, *ibid,* **56**, 2415 (1986); F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998).

[3] V. Galitskii and A. Migdal, Soviet Phys-JEPT **7**, 96 (1958).

[4] B.I. Lundqvist, Phys. Kondens. Materie **6**, 206 (1967); B. I. Lundqvist and V. Samathiyakatanit, *ibid,* **9**, 231 (1969).

[5] E.L. Shirley, Phys. Rev. B **54**, 7758 (1996).

[6] B. Holm, Phys. Rev. Lett. **83**, 788 (1999); B. Holm and U. von Barth, Phys. Rev. B **57**, 2108 (1998).

[7] W. Kohn and L.J. Sham, Phys. Rev. **140**, A1133 (1965).

[8] W. Kohn, Y. Meir, and D. E. Makarov, Phys. Rev. Lett. **80**, 4153 (1998); J.F. Dobson and J. Wang, *ibid,* **82**, 2123 (1999).

[9] J. Grossman and L. Mitas, Phys. Rev. Lett. **79**, 4353 (1997).

[10] W. Leung, R.J. Needs, and G. Rajagopal, Phys. Rev. Lett. **83**, 2351 (1999).

[11] Y. Kim, I. Lee, S. Nagaraja, J.P. Leburton, R.Q. Hood, and R.M. Martin, Phys. Rev. B **61**, 5202 (2000); P. García-González, *ibid* **62**, 2321 (2000).

[12] W.M.C. Foulkes, L. Mitas, G. Rajagopal, and R.J. Needs, Rev. Mod. Phys. (to be published).

[13] N.H. Rojas, R.W. Godby, and R.J. Needs, Phys. Rev. Lett. **74**, 1827 (1995).

[14] M.M. Rieger, L. Steinbeck, I.D. White, N.H. Rojas, and R.W. Godby, Comput. Physics

Commun. **117**, 211 (1999); L. Steinbeck, A. Rubio, L. Reining, M. Torrent, I.D. White, and R.W. Godby, *ibid*, **125**, 105 (2000).

[15] Note that $\Delta\mu = \mu - \mu_0$, where μ_0 is the chemical potential of the fictitious system under the potential v_0 alone.

[16] The factor 2 in Eq. 4 comes out after a sum over the spin variable in spin-unpolarized systems. For spin-polarized systems such sum has to be done explicitly.

[17] A. Schindlmayr, Phys. Rev. B **56**, 3528 (1997).

[18] G. Baym and L.P. Kadanoff, Phys. Rev. **124**, 287 (1961).

[19] G. Baym, Phys. Rev. **127**, 1391 (1962).

[20] U. von Barth and B. Holm, Phys. Rev. B **54**, 8411 (1996).

[21] W.D. Schöne and A.G. Eguiluz, Phys. Rev. Lett. **81**, 1662 (1998).

[22] M. Hindgren, Ph.D. Thesis, University of Lund, 1997 (unpublished); U. von Barth (private communication).

[23] D.M. Ceperley and B.J. Adler, Phys. Rev. Lett. **45**, 566 (1980)

[24] G. Ortiz, M. Harris, and P. Ballone, Phys. Rev. Lett. **82**, 5317 (1999); G. Ortiz and P. Ballone, Phys. Rev. B **50**, 1391 (1994).

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

[26] B. Tanatar and D. M. Ceperley, Phys. Rev. B **39**, 5005 (1989); Y. Kwon, D. M. Ceperley and R. Martin, *ibid,* **48**, 12037 (1993).

[27] M.M. Rieger and R.W. Godby, Phys. Rev. B **58**, 1343 (1998).

TABLES

r_s	1	2	4	5	10	20
QMC	0.5180	0.2742	0.1464	0.1197	0.0644	0.0344
	0.5127	0.2713		0.1201		0.0344
GW	0.5160(2)	0.2727(5)	0.1450(5)	0.1185(5)	0.0620(9)	0.032(1)
		0.2741	0.1465			
GW_0	0.5218(1)	0.2736(1)	0.1428(1)	0.1158(1)	0.0605(4)	0.030(1)
G_0W_0	0.5272(1)	0.2821(1)	0.1523(1)	0.1247(1)	0.0665(2)	0.0363(5)
RPA	0.5370	0.2909	0.1613	0.1340	0.0764	0.0543
$-\varepsilon_X$	0.4582	0.2291	0.1145	0.0916	0.0458	0.0229

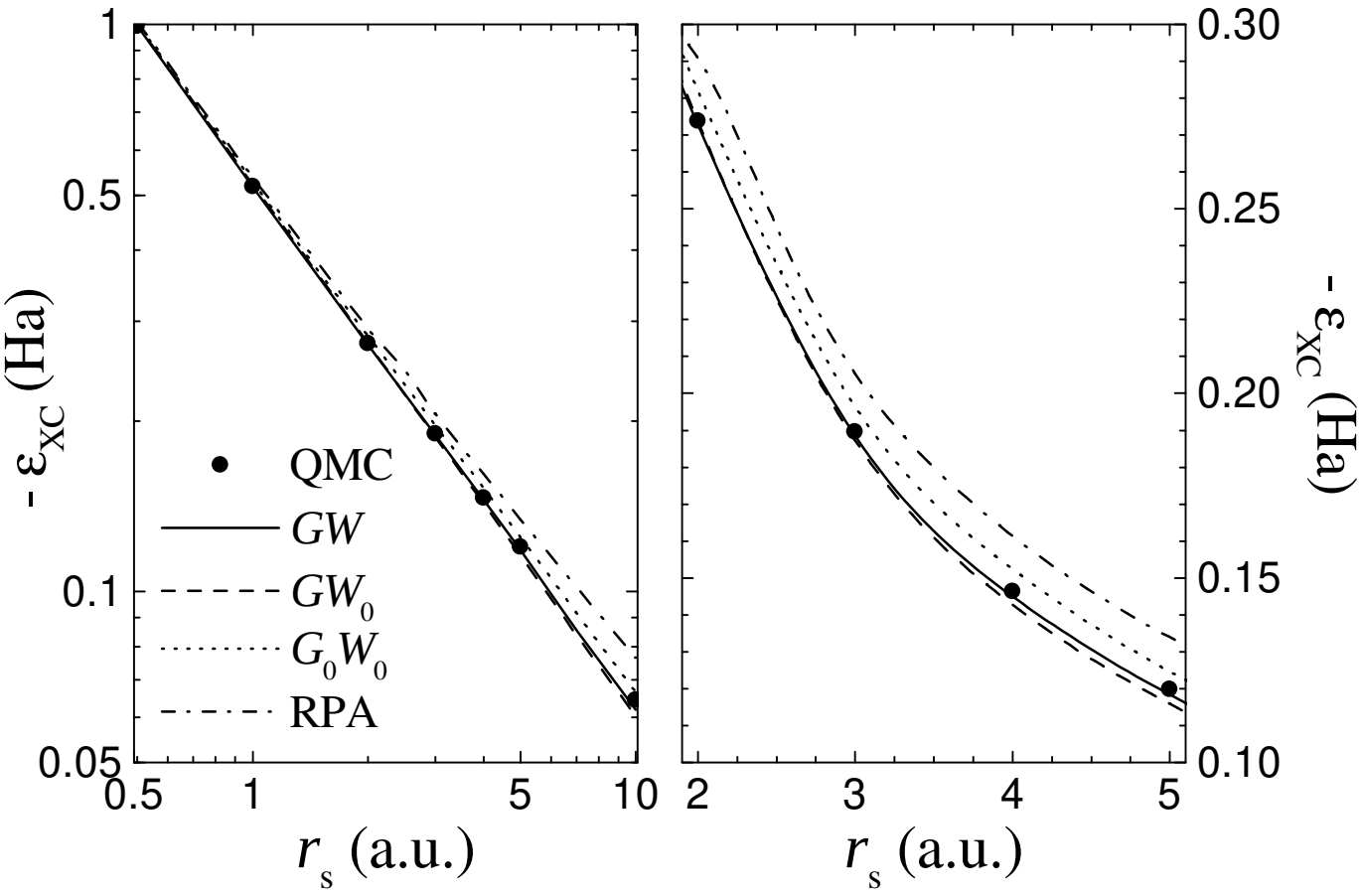
TABLE I. Minus XC energies per particle (in Hartrees) for the spin-unpolarized phase of the 3D homogeneous electron gas obtained through several GW schemes. The second row in the GW entry corresponds to Ref. [6]. Also shown are the RPA results, and the QMC values from Ref. [23] (first row) and from Ref. [24] (second row). Parenthesis indicates the numerical uncertainty in the last significant figure. For reference, the exchange energy per particle, ε_X, is included.

FIGURES

FIG. 1. XC energy per particle, $\varepsilon_{\rm XC}$, for the spin-unpolarized 3D homogeneous electron gas. The essentially exact Monte Carlo results (symbols) are compared with several GW schemes (lines). The excellent performance of the self-consistent GW and (to a lesser extent) the partially self-consistent GW_0, is evident. Note that the differences between several Monte-Carlo results are less than the symbols size.

FIG. 2. As Fig. 1, for the fully spin-polarized ($\chi = 1$) phase of the 3D electron gas.

FIG. 3. As in Fig. 1, for the spin-unpolarized 2D electron gas.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0.1
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10
- ε_XC (Ha)
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QMC
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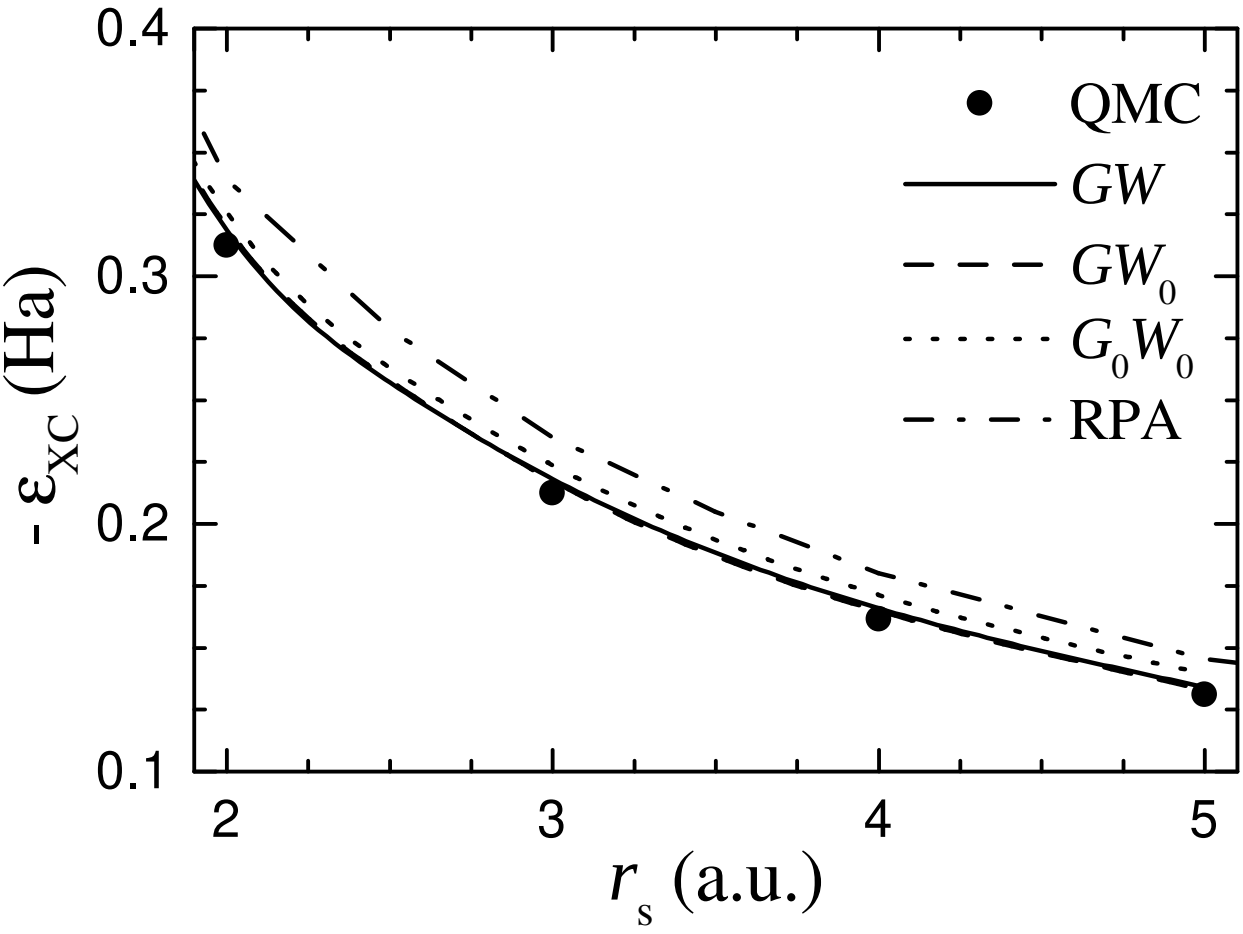
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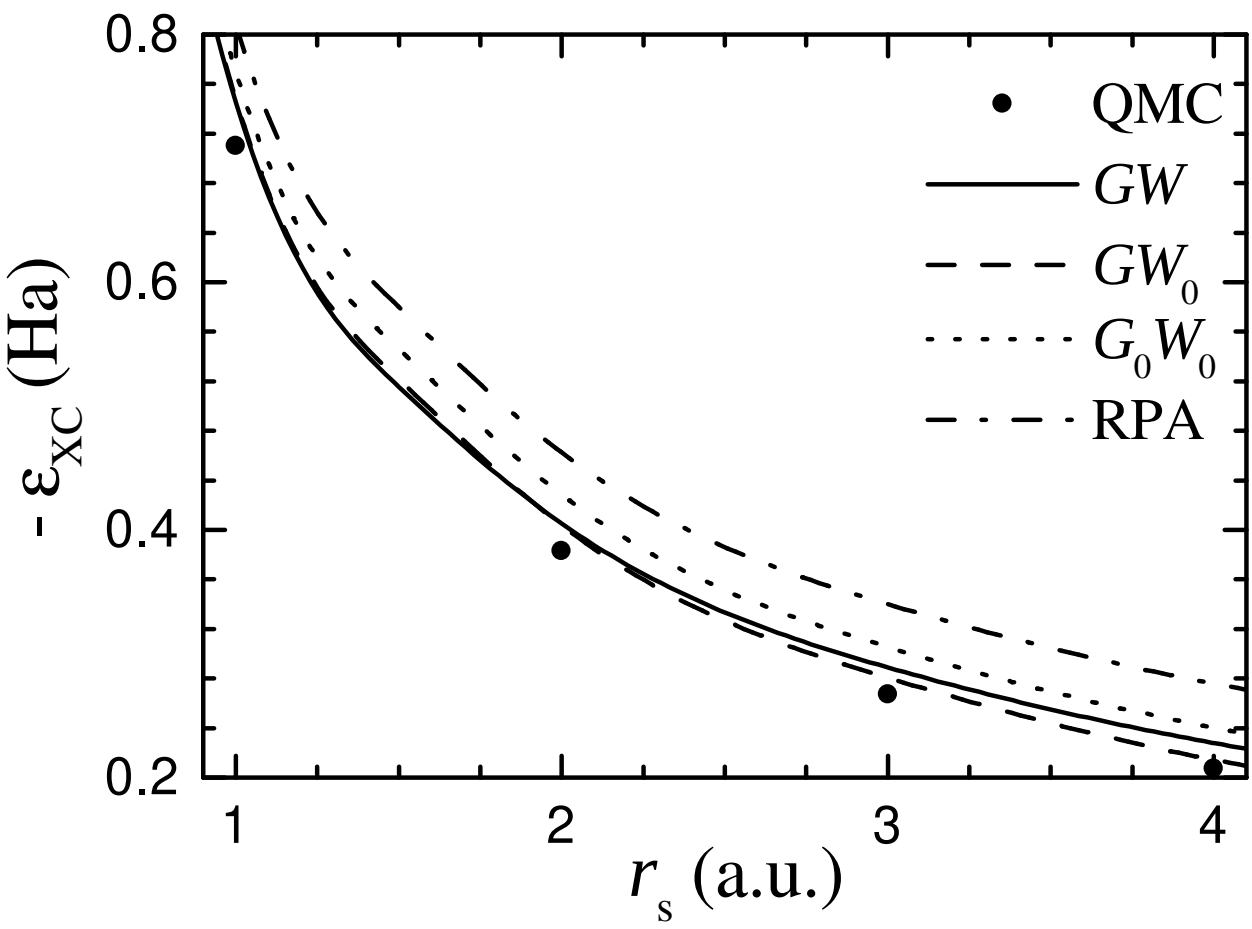
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- ε_XC (Ha)
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