View metadata, citation and similar papers at core.ac.uk

brought to you by CORE

provided by Warwick Research Archives Portal Repository

WARWICK
THE UNIVERSITY OF WARWICK

Original citation:

Wood, B., Hine, Nicholas, Foulkes, W. M. C. and Garcia-Gonzalez, P.. (2007) Quantum Monte Carlo calculations of the surface energy of an electron gas. Physical Review B (Condensed Matter and Materials Physics), 76 (3). 035403.

Permanent WRAP URL:

http://wrap.warwick.ac.uk/78159

Copyright and reuse:

The Warwick Research Archive Portal (WRAP) makes this work by researchers of the University of Warwick available open access under the following conditions. Copyright © and all moral rights to the version of the paper presented here belong to the individual author(s) and/or other copyright owners. To the extent reasonable and practicable the material made available in WRAP has been checked for eligibility before being made available.

Copies of full items can be used for personal research or study, educational, or not-for-profit purposes without prior permission or charge. Provided that the authors, title and full bibliographic details are credited, a hyperlink and/or URL is given for the original metadata page and the content is not changed in any way.

Publisher statement:

© 2007 American Physical Society

A note on versions:

The version presented here may differ from the published version or, version of record, if you wish to cite this item you are advised to consult the publisher's version. Please see the 'permanent WRAP URL' above for details on accessing the published version and note that access may require a subscription.

For more information, please contact the WRAP Team at: wrap@warwick.ac.uk

warwick.ac.uk/lib-publications

PHYSICAL REVIEW B **76**, 035403 (2007)

Quantum Monte Carlo calculations of the surface energy of an electron gas

B. Wood, N. D. M. Hine, and W. M. C. Foulkes
Department of Physics, Imperial College London, Exhibition Road, London SW7 2AZ, United Kingdom

P. García-González
Departamento de Física Fundamental, Universidad Nacional de Educación a Distancia, Apartado 60.141, E-28080 Madrid, Spain

(Received 5 June 2007; published 5 July 2007)

We present quantum Monte Carlo calculations of the surface energy of the electron gas (jellium). Our results agree with the best estimates obtained by other methods, thus appearing to resolve the controversy which currently exists and paving the way for future simulations of real surface systems.

DOI: 10.1103/PhysRevB.76.035403 PACS number(s): 73.20.−r, 71.10.Ca, 71.15.−m, 02.70.Ss

I. INTRODUCTION

Surfaces mediate all our interactions with the world and play a vital role in many significant technological and natural processes. Understanding the physics of surfaces is therefore of great importance. The simplest surface, that of the model electron gas ("jellium"), provides one of the canonical problems in computational electronic structure: from density-functional theory[1] (DFT) and the Fermi hypernetted-chain method[2,3] to the GW approximation[4] and quantum Monte Carlo simulations,[5,6] the jellium surface has been a standard proving ground.

Since the first quantum Monte Carlo (QMC) simulations were performed nearly 15 years ago, it has also been a source of controversy, highlighted recently in several papers.[7–12] Many different authors have calculated the surface energy of jellium using methods based on DFT or the random-phase approximation (RPA) or a combination of the two;[1,13–16] their results show broad agreement with each other while disagreeing with the QMC results.[5,6] Most surface energy calculations are based on simulations of slabs, but other methods exist; QMC simulations of finite jellium spheres[17] have been combined with a liquid-drop model[18] to calculate the surface energy. These results are also consistent with those from DFT- and RPA-based methods but not with the conventional supercell QMC calculations. The difference is typically of the order of 150 erg cm^{-2}, comparable with the magnitude of the surface energy itself. A previous paper[8] aimed to resolve the controversy, pointing out an error in one set of the QMC calculations; we will show that there are other more important reasons for the discrepancy. This is very significant because QMC, and, in particular, diffusion Monte Carlo (DMC), is often considered to be the most accurate method available and is used as a benchmark. If QMC calculations were shown to be wrong for this model system, serious doubt would be cast on this status. On the other hand, if the QMC results were proven correct, there would be even more serious consequences: a good deal of surface-science theory would have to be reexamined.

In this paper, we examine the challenges involved in calculating surface energies and show how to meet them. We explain why we believe that the previous QMC simulations did not attain the unusually high precision required for these calculations (energy differences accurate to within 0.03 mHa per electron) and present results which appear to resolve the longstanding controversy. This allows us to have confidence in the results of future simulations of surfaces.[19]

II. BACKGROUND

Jellium consists of electrons moving over a fixed background of uniform positive charge, so that on average the system is neutral. A surface is formed by abruptly terminating the background charge; electrons then spill out slightly, with the electron density decreasing smoothly to zero. The surface energy is the energy per unit area required to create a surface at zero temperature. Surface energy calculations are usually based on simulations of a slab (with two surfaces), where the background charge density has the form of a top hat. In a slab, we can write the energy per electron as

$$\varepsilon_{\mathrm{slab}} = \varepsilon_{\mathrm{bulk}} + 2\left(\frac{4\pi r_s^3}{3s}\right)\sigma, \tag{1}$$

where σ is the surface energy and $\varepsilon_{\mathrm{bulk}}$ is the energy per electron in the bulk system. The term in brackets is the in-plane area per electron: s is the slab width, while r_s is the conventional density parameter. (In the bulk system, each electron occupies an average volume $4\pi r_s^3/3$; r_s will always be quoted in a.u.) With this definition, the surface energy is an oscillatory function of the slab width[9] because of the communication between the two surfaces of the slab; the oscillations decay as the slab gets wider, and the true surface energy is $\lim_{s\to\infty}\sigma(s)$. Figure 1 shows the form of $\sigma(s)$ for two densities, calculated using DFT with the local density approximation (LDA). The period of the oscillations in σ is half the Fermi wavelength (and therefore proportional to r_s).[9]

Correctly extrapolating to the infinite-s limit is one of the major difficulties facing any method based on a slab calculation. Another is the extraordinary level of accuracy required; the surface energy of jellium becomes negative at high densities,[1] while at intermediate densities, the kinetic, electrostatic, and exchange-correlation components of the surface energy are all individually large but almost cancel out. For reasonable slab widths at these densities, an error of 0.5 mHa in $\varepsilon_{\mathrm{bulk}}$ can lead to an error of 150 erg cm^{-2} in the calculated surface energy. If we make s larger, the situation gets worse; if we make it smaller, the oscillations in σ become more of a problem. The extreme sensitivity to errors

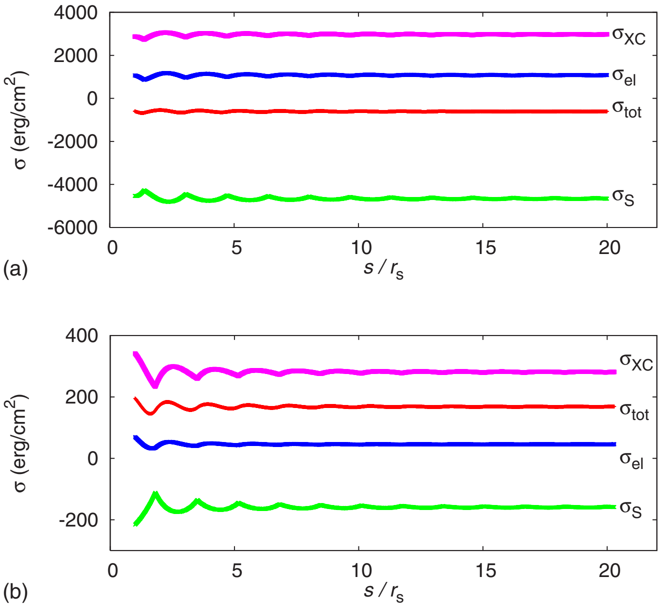

FIG. 1. (Color online) The components of the jellium surface energy for (a) r_s=2.07 and (b) r_s=3.94, calculated from Eq. (1) using the LDA. The total surface energy is σ_{tot}, which is the sum of kinetic (σ_S), electrostatic (σ_{el}), and exchange-correlation (σ_{XC}) terms. Note the cancellation between different components of the total energy, especially for r_s=2.07.

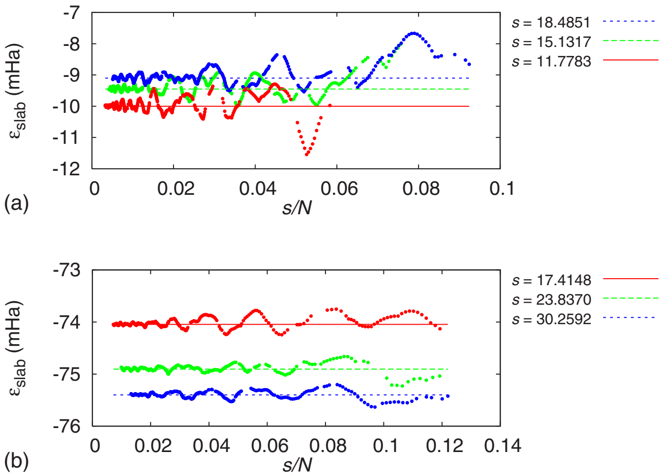

FIG. 2. (Color online) The total energy per electron $\varepsilon_{\text{slab}}$, calculated for a finite cell using the LDA with (a) r_s=2.07 and (b) r_s=3.94. N is the number of electrons. For a given density, the abscissa is inversely proportional to the in-plane area of the cell because $s/N=4\pi r_s^3/3L^2$. The horizontal lines are the infinite-L limits. The slab widths are chosen so that the infinite-cell surface energy (as calculated in the LDA) matches the infinite-cell, infinite-s limit. The finite-cell errors are more severe when r_s=2.07, which means that we are forced to use larger cells at this density.

means that comparing the results of simulations of two entirely different systems—bulk and slab—is dangerous.[20,21] This applies equally to DFT and QMC calculations; we believe that it is more severe in the case of QMC and that this caused the previous QMC calculations to be inaccurate. For high accuracy, cancellation of errors is vital, and below we will describe a method which does not rely on bulk calculations at all.

In DFT, we can exploit the in-plane symmetry of the slab system to make the calculation effectively one dimensional. This is not possible in QMC, where every real electron is represented in the simulation; QMC simulations must therefore use a finite simulation cell. We choose the in-plane profile of the cell to be a square of side L. The consequent in-plane finite-size errors are significant and decay slowly with L; this is illustrated in Fig. 2, where we again plot the results of LDA calculations. Unless explicitly stated otherwise, we work in a.u. throughout. This time, we choose not to perform the analytical in-plane integration and instead use a finite cell, as in QMC. In QMC, there are additional errors,[22] comparable in size, possibly due to "squashing" of the exchange-correlation hole into the finite simulation cell. The nature of these in-plane finite-size errors was not understood when the previous QMC simulations were performed. It is not sufficient to work with only a single value of L.

To explain why the comparison of slab and bulk systems generates more serious errors in QMC than in DFT, we must look in more detail at the key approximations in the two methods. At the heart of DFT is the exchange-correlation energy functional, which is unknown and must be approximated. The simplest approach is to use the LDA, which one would naively expect to be adequate for slowly varying electron densities and inadequate otherwise; however, in many situations of the latter type, including the jellium surface, there is a demonstrable cancellation of errors and it continues to work remarkably well.[10]

DMC is a statistical method for projecting out the ground-state component of a many-particle trial wave function.[23] When applied to many-electron systems, the well-known fermion sign problem motivates the use of the fixed-node approximation. Instead of the true ground state, the method then projects out the lowest-energy state with the same nodal surface as the trial wave function. (The nodal surface is the set of points where the wave function is zero.) The fixed-node approximation introduces a small error in the total energy, which we believe is different for bulk and slab simulations; the nodal surface of the trial wave function is closer to that of the true ground state in the bulk system than it is in the slab. Although the difference in errors is very small, the sensitive nature of the problem means that it (along with the very slow convergence in L) is the major source of inaccuracy in previous QMC calculations. We will return to this point later and justify this assessment with reference to our results.

The release-node algorithm[24] and the use of backflow correlations[25,26] can overcome the fixed-node limitation but at a high computational cost. In order to deal with the slowly decaying in-plane finite-size errors, we are forced to use very large simulation cells containing hundreds and sometimes thousands of electrons; this makes using the release-node algorithm or backflow correlations impractical.

III. METHOD

Having outlined the many problems associated with calculating the jellium surface energy, in particular, in QMC, we

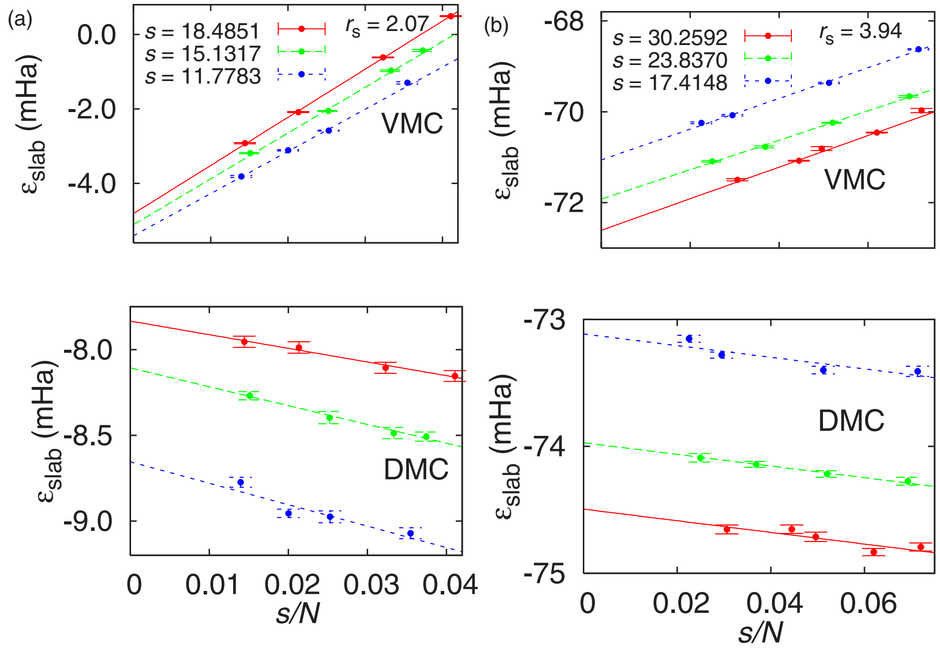

FIG. 3. (Color online) The energy per electron in QMC, as a function of the in-plane cell size, for (a) $r_s=2.07$ and (b) $r_s=3.94$.

now describe our methods for overcoming them. We can avoid the comparison between slab and bulk systems by calculating $\varepsilon_{\mathrm{slab}}$ for several different slab widths[20,21] and fitting the results to the formula (1). We mitigate the effect of the oscillations in σ by choosing slab widths for which the LDA surface energy matches the infinite-s limit.

For each density, our method for obtaining the surface energy is therefore the following:

(1) We perform infinite-cell DFT calculations, using the LDA and the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA),[27] for a range of slab widths, as shown in Fig. 1.

(2) We then choose three special slab widths: consecutive values of s for which (within the infinite-cell LDA) $\sigma(s)=\lim_{s'\to\infty}\sigma(s')$.

(3) For each slab width, we carry out DFT, QMC, and RPA simulations over a range of in-plane cell sizes (values of L) to obtain values of $\varepsilon_{\mathrm{slab}}$. We choose our values of L so that the energy per electron for the finite cell, as calculated in the LDA, closely matches the infinite-cell value; this reduces the in-plane finite-size errors. We could use arbitrary values of L and apply a standard correction of the form $\varepsilon_{\mathrm{slab}}^{\mathrm{LDA}}(\infty)-\varepsilon_{\mathrm{slab}}^{\mathrm{LDA}}(L)$; using special values gives marginally better convergence.

(4) We plot $\varepsilon_{\mathrm{slab}}$ against s/N (which is inversely proportional to the in-plane cell area) for the three slab widths. We should obtain three straight lines; we can then extrapolate our results to the infinite-L limit.

(5) We plot the extrapolated values of $\varepsilon_{\mathrm{slab}}$ against $1/s$; according to Eq. (1), this should generate a straight line from whose gradient we can calculate the surface energy.

We perform variational Monte Carlo (VMC) as well as DMC simulations; these are less computationally expensive but less accurate because VMC is not a projector method. We generate the trial wave functions for the QMC calculations by combining a Slater determinant of LDA or GGA single-particle wave functions with a short-ranged Jastrow factor of the form described in Ref. 28. The Jastrow factor is separately optimized for each system size.

We have calculated the jellium surface energy for a range of densities from $r_s=2.07$ to $r_s=3.94$. The QMC simulations were carried out using the CASINO program.[29] Coulomb interactions were incorporated by using the quasi-two-dimensional version of the model periodic Coulomb interaction,[22,30] which is faster than the corresponding Ewald sum and equally accurate.[22]

In the previous QMC calculations, the full three-dimensional Ewald sum was used, so that the system was effectively not an isolated slab but one slab in an infinitely repeated periodic array; however, we do not believe that this had a significant effect on the final results.

IV. RESULTS

Figure 3 shows the raw QMC data. In QMC, convergence with respect to the in-plane cell size is slow; the DMC results show the expected negative finite-size error,[22] although the error is positive for VMC. This is because the Jastrow factor (which plays a significant role in determining electron-electron correlations in VMC) is better for larger systems. However, despite the slow convergence of the energy per electron in both VMC and DMC, we can see that each set of data lies on a straight line; the intersection of these lines with the vertical axis gives us the extrapolated value of $\varepsilon_{\mathrm{slab}}$. The largest systems we studied had $N\sim1000$ (in DMC) and $N\sim2600$ (in VMC).

We use the extrapolated values of $\varepsilon_{\mathrm{slab}}$ to generate Fig. 4. The gradient of this new line is proportional to the surface energy. RPA and RPA+ results are also shown. RPA+ combines the RPA with a correction to the short-range electron-electron correlation;[14] the correction we use is derived from the LDA.

Table I, illustrated in Fig. 5, is the central result of this work. It shows the jellium surface energy, comparing DFT,

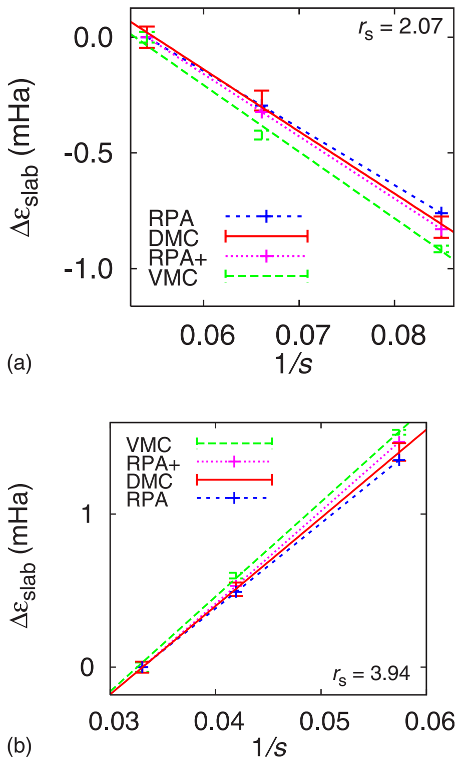

FIG. 4. (Color online) The difference $\Delta\varepsilon_{\mathrm{slab}}$ in the energy per electron in slabs of different widths, for (a) r_s=2.07 and (b) r_s=3.94. The QMC results (extrapolated to the infinite-L limit) are compared with those from the RPA and RPA+.

QMC, and RPA calculations. QMC is based on pseudorandom sampling and therefore generates results which are inherently subject to statistical uncertainty. Fortunately, the size of the statistical error is easy to estimate;[31] the error bars shown in Fig. 3 are derived in this way. By fitting $\varepsilon_{\mathrm{slab}}$ to a linear function of s/N and then fitting the extrapolated (to infinite cell size or $s/N \to 0$) values of $\varepsilon_{\mathrm{slab}}$ to a linear function of s, we also introduce systematic errors—because these functions are not truly linear. In Figs. 4 and 5 and in Table I, the errors shown include both statistical and systematic components obtained from a standard regression analysis. The final errors in the surface energy are dominated by the systematic contributions.

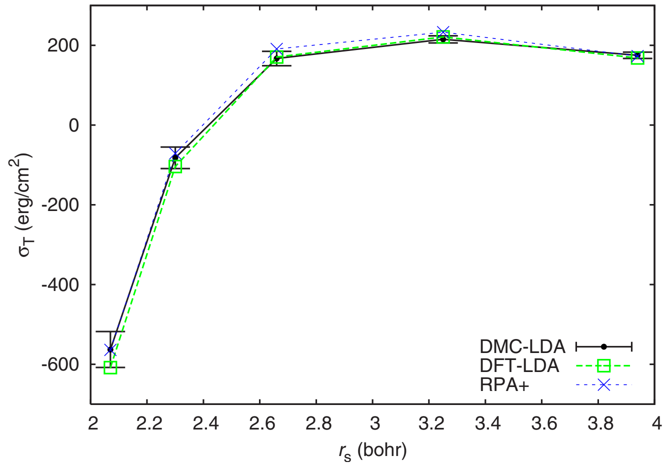

FIG. 5. (Color online) The surface energy of jellium as a function of density. The points correspond approximately to the electron densities of a range of metals: r_s=2.07 (Al), 2.30 (Zn), 2.66 (Mg), 3.25 (Li), and 3.94 (Na).

The DMC results are consistent with those obtained with the LDA and RPA+. They are not consistent with our GGA, RPA, or VMC values. Several comparisons of the jellium surface energy obtained by different methods exist in the literature;[10,12,32] the general trend is that

$$\sigma_{\mathrm{GGA}} < \sigma_{\mathrm{LDA}} < \sigma_{\mathrm{mGGA}} < \sigma_{\mathrm{RPA+}} < \sigma_{\mathrm{RPA}}, \qquad (2)$$

where mGGA stands for meta-GGA. Our DMC results are broadly consistent with the LDA, mGGA, and RPA+, values lying closer to RPA+ for high densities and to LDA for low densities.

Reassuringly, the choice of density functional used to generate the trial wave functions (LDA or GGA) does not appear to affect the DMC surface energy. To test the effectiveness of our method of selecting three slab widths for each density, we compare the RPA results obtained this way with the corresponding "converged" RPA values (including simulations of wider slabs, which are impractical in QMC), denoted RPAc. The differences are small; this gives us confidence in our method.

As an additional test, we perform our own DMC simulations of bulk jellium and calculate the surface energy in the traditional way—by direct comparison of bulk and slab results. We use values for the energy per electron which are converged with respect to L (for the slabs) and to the system size (for the bulk systems). The results are shown in Table II; the surface energy values we obtain for different slab widths do not agree with each other. The extent to which they dis-

TABLE I. The jellium surface energy (in erg cm^{-2}). The labels in brackets indicate the approximation scheme used to generate the orbitals for the QMC trial wave function.

r_s (bohr)	LDA	GGA	VMC (LDA)	DMC (LDA)	DMC (GGA)	RPA+	RPA	RPAc
2.07	−608.2	−690.6	−637±50	−563±45		−564	−517	−506
2.30	−104.0	−164.1	−131±40	−82±27		−71	−34	−25
2.66	170.6	133.0	200±11	179±13	158±26	191	216	225
3.25	221.0	201.2	252±14	216±8		233	248	253
3.94	168.4	158.1	188±3	175±8	169±9	173	182	187

TABLE II. The jellium surface energy (in erg cm^{-2}), comparing direct calculations with our extrapolation method. The slab widths s_1, s_2, and s_3 are density dependent; for each density, they are approximately uniformly spaced. The spacing is proportional to r_s; the ordering is $s_1 < s_2 < s_3$.

r_s (bohr)	ε_b (mHa)	$\sigma(s_1)$	$\sigma(s_2)$	$\sigma(s_3)$	Extrapolated σ
2.07	−6.48±0.14	−536±42	−516±46	−524±56	−563±45
2.30	−31.39±0.15	−52±31	−50±39	−33±49	−82±27
2.66	−54.63±0.13	224±15	243±21	256±26	179±13
3.25	−71.34±0.07	254±6	267±8	284±11	216±8
3.94	−76.75±0.06	194±5	200±4	208±9	175±8

agree allows us to estimate the difference in size of the fixed-node error in the energy per electron between bulk and slab systems; this is of the order of 1 mHa per electron and does not decrease as s increases (as one would expect for a "surface" effect) but remains approximately constant for the slab widths studied here. Consequently, the best direct estimates of the surface energy are obtained from simulations of thin slabs. For comparison, Fig. 3 shows that the in-plane finite-size error is typically around 0.3 mHa per electron.

We note that the QMC simulations of jellium spheres carried out by Sottile and Ballone[17] did not suffer from large fixed-node errors; the authors were able to check that the nodal surface was optimized by using a wave function made up of a linear combination of Slater determinants.

V. CONCLUSION

We have investigated the problem of calculating surface energies in QMC. We have shown that great care must be taken to control the finite-size errors associated with both the width of the slab and the in-plane size of the cell. Comparing bulk and slab calculations is to be avoided: the cancellation of errors that works so well in DFT is less reliable in QMC. We believe that our method—performing simulations at three specially selected slab widths and then extrapolating—gives more reliable results. Our results reconcile the previous differences between QMC and DFT calculations of the jellium surface energy and provide a template for future work on real surfaces.

ACKNOWLEDGMENTS

The DMC simulations made use of the facilities of the Imperial College High Performance Computing Service and of HPCx, the UK's national high-performance computing service, which is provided by EPCC at the University of Edinburgh and by CCLRC Daresbury Laboratory and funded by the Office of Science and Technology through EPSRC's High End Computing Programme. P.G.-G. acknowledges financial support by the Spanish MEC through the Ramon y Cajal Program and Project No. FIS2004-05035-C03-03.

---

[1] N. D. Lang and W. Kohn, Phys. Rev. B **1**, 4555 (1970).
[2] E. Krotscheck, W. Kohn, and G.-X. Qian, Phys. Rev. B **32**, 5693 (1985).
[3] E. Krotscheck and W. Kohn, Phys. Rev. Lett. **57**, 862 (1986).
[4] A. G. Eguiluz, M. Heinrichsmeier, A. Fleszar, and W. Hanke, Phys. Rev. Lett. **68**, 1359 (1992).
[5] X. P. Li, R. J. Needs, R. M. Martin, and D. M. Ceperley, Phys. Rev. B **45**, 6124 (1992).
[6] P. H. Acioli and D. M. Ceperley, Phys. Rev. B **54**, 17199 (1996).
[7] J. M. Pitarke and A. G. Eguiluz, Phys. Rev. B **57**, 6329 (1998).
[8] J. M. Pitarke, Phys. Rev. B **70**, 087401 (2004).
[9] J. M. Pitarke and A. G. Eguiluz, Phys. Rev. B **63**, 045116 (2001).
[10] Z. Yan, J. P. Perdew, S. Kurth, C. Fiolhais, and L. Almeida, Phys. Rev. B **61**, 2595 (2000).
[11] L. A. Constantin, J. P. Perdew, and J. Tao, Phys. Rev. B **73**, 205104 (2006).
[12] V. N. Staroverov, G. E. Scuseria, J. Tao, and J. P. Perdew, Phys. Rev. B **69**, 075102 (2004).
[13] J. P. Perdew, S. Kurth, A. Zupan, and P. Blaha, Phys. Rev. Lett. **82**, 2544 (1999).
[14] S. Kurth and J. P. Perdew, Phys. Rev. B **59**, 10461 (1999).
[15] D. C. Langreth and J. P. Perdew, Phys. Rev. B **15**, 2884 (1977).
[16] J. M. Pitarke, L. A. Constantin, and J. P. Perdew, Phys. Rev. B **74**, 045121 (2006).
[17] F. Sottile and P. Ballone, Phys. Rev. B **64**, 045105 (2001).
[18] L. M. Almeida, J. P. Perdew, and C. Fiolhais, Phys. Rev. B **66**, 075115 (2002).
[19] D. Alfè and M. J. Gillan, J. Phys.: Condens. Matter **18**, L435 (2006).
[20] J. C. Boettger, Phys. Rev. B **49**, 16798 (1994).
[21] V. Fiorentini and M. Methfessel, J. Phys.: Condens. Matter **8**, 6525 (1996).
[22] B. Wood, W. M. C. Foulkes, M. D. Towler, and N. D. Drummond, J. Phys.: Condens. Matter **16**, 891 (2004).
[23] B. L. Hammond, W. A. Lester, Jr., and P. J. Reynolds, *Monte Carlo Methods in Ab Initio Quantum Chemistry* (World Scientific, Singapore, 1994).
[24] D. M. Ceperley and B. J. Alder, Phys. Rev. Lett. **45**, 566 (1980).
[25] Y. Kwon, D. M. Ceperley, and R. M. Martin, Phys. Rev. B **48**, 12037 (1993).

[26] Y. Kwon, D. M. Ceperley, and R. M. Martin, Phys. Rev. B **58**, 6800 (1998).

[27] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[28] B. Wood and W. M. C. Foulkes, J. Phys.: Condens. Matter **18**, 2305 (2006).

[29] R. J. Needs, M. D. Towler, N. D. Drummond, and P. R. C. Kent, *CASINO Version 1.7 User Manual* (University of Cambridge, Cambridge, 2004).

[30] A. J. Williamson, G. Rajagopal, R. J. Needs, L. M. Fraser, W. M. C. Foulkes, Y. Wang, and M. Y. Chou, Phys. Rev. B **55**, R4851 (1997).

[31] H. Flyvbjerg and H. G. Petersen, J. Chem. Phys. **91**, 461 (1989).

[32] S. Kurth, J. P. Perdew, and P. Blaha, Int. J. Quantum Chem. **75**, 889 (1999).