

Efficient, long-range correlation from occupied wavefunctions only

Tim Gould* and John F. Dobson

QLD Micro- and Nanotechnology Centre, Griffith University, Nathan, QLD 4111, Australia

(Dated: June 23, 2011)

We use continuum mechanics [Tao *et al*, PRL**103**,086401] to approximate the dynamic density response of interacting many-electron systems. Thence we develop a numerically efficient exchange-correlation energy functional based on the Random Phase Approximation (dRPA). The resulting binding energy curve $E(D)$ for thin parallel metal slabs at separation D better agrees with full dRPA calculations than does the Local Density Approximation. We also reproduce the correct non-retarded van der Waals (vdW) power law $E(D) \approx -C_{5/2}D^{-5/2}$ as $D \rightarrow \infty$, unlike most vdW functionals.

PACS numbers: 73.22.-f,31.15.E-,74.25N-,34.20.Gj

An increasing body of work[1–4] has demonstrated that the correlation energy E_c^{dRPA} in the direct Random-Phase Approximation (dRPA) is highly accurate for energy differences in many and varied electronic systems, at least in cases where orbital self interaction is not an issue. dRPA binding properties for a wide variety of bulk materials[2] are typically more accurate than those from the local density approximation (LDA), especially for dispersion (van der Waals, vdW) bound systems[3]. For the vdW attractive potential, which is totally neglected in the LDA, the dRPA proves to be versatile, predicting unusual vdW coefficients[5] and power laws[6] in agreement with quantum Monte Carlo results[7].

E_c^{dRPA} is typically obtained in three steps: i) The bare response $\hat{\chi}_0$ is obtained from occupied and unoccupied groundstate wavefunctions. This is typically the numerical bottleneck. Recent developments[8] attempt to bypass unoccupied states but will not work for metallic systems. ii) The interacting response is calculated through the dRPA as $\hat{\chi}_\lambda(\omega) = \hat{\chi}_0(\omega) + \lambda\hat{\chi}_0(\omega)\hat{v}\hat{\chi}_\lambda(\omega)$ where \hat{v} is the Coulomb potential $|\mathbf{r} - \mathbf{r}'|^{-1}$. iii) Finally the correlation energy is calculated through the Adiabatic Connection and Fluctuation Dissipation Theorem (ACFDT) approach

$$E_c^{\text{dRPA}} = - \int_0^\infty \frac{d\omega}{2\pi} \text{Tr} \left[\log[\hat{1} - \hat{A}(\omega)] + \hat{A}(\omega) \right] \quad (1)$$

where $\hat{A}(\omega) = \hat{v}^{1/2}\hat{\chi}_0(\omega)\hat{v}^{1/2}$ is an Hermitian operator[9].

Other efficient van der Waals functionals[10, 11] give good results for many systems. However they represent E_c^{vdW} in an additive two-point approximation that is either obtained semi-empirically[10] or derived[11] by solving the dynamical screening problem (1) perturbatively. As a result, these functionals miss non-pairwise-additive vdW energy contributions that can be substantial in highly polarizable, highly anisotropic systems[5, 6], including low-dimensional metals.

Here we solve equation (1) accurately thus avoiding the pairwise additive approximation, but we use the continuum mechanics of Tokatly, Tao, Gao and Vignale (TTGV)[12, 13] to approximate $\hat{\chi}_0$ in a numerically effi-

cient manner. A conceptually similar approach was taken in [14] but the direct scheme for $\hat{\chi}_0$ used there was numerically inefficient and even ambiguous in general geometries. TTGV rigorously define a relationship between the change in density and the external potential utilising groundstate properties only. Their method is appropriate in the high-frequency and low-wavenumber limit for all electronic systems and gives[13] the correct excitation frequencies Ω_N of quantal one-electron systems.

The TTGV scheme uses the continuum fluid displacement \mathbf{u} , which is related to the density perturbation n^1 by[13, 15]

$$n^1(\mathbf{r}, t) = -\partial_\mu [n^0(\mathbf{r})u_\mu(\mathbf{r}, t)]. \quad (2)$$

For a small change to the KS potential $V^1(\mathbf{r}, t)$ we can approximate \mathbf{u} through the following hydrodynamic-like equation (from equations 3, 4 and 14-16 of [13])

$$\partial_{tt}u_\mu(\mathbf{r}, t) = -\partial_\mu V^1(\mathbf{r}, t) - \Phi_{\mu\nu}^0 u_\nu(\mathbf{r}, t) + \frac{F_\mu^0(\mathbf{r}, t)}{n^0(\mathbf{r})} \quad (3)$$

where $n^0(\mathbf{r})$, $\Phi_{\mu\nu}^0 = [\partial_{\mu\nu} V^{\text{KS}}(\mathbf{r})]$ and $F_\mu^0(\mathbf{r}, t)$ are groundstate properties of the system.

The force F_μ^0 defined in equation 14 of [13] can be written as a linear Hermitian operator acting on the displacement vector through $F_\mu^0 = -\hat{K}_{\mu\nu} u_\nu(\mathbf{r}, t)$. Here

$$\hat{K}_{\mu\nu} = \hat{K}_{\mu\nu}^{(T)} - \frac{1}{4}\hat{K}_{\mu\nu}^{(n)} \quad (4)$$

$$\hat{K}_{\mu\nu}^{(T)} = \partial_\alpha \bar{T}_{\mu\nu}^0 \partial_\alpha + \partial_\nu \bar{T}_{\mu\alpha}^0 \partial_\alpha + \partial_\alpha \bar{T}_{\alpha\nu}^0 \partial_\mu \quad (5)$$

$$\hat{K}_{\mu\nu}^{(n)} = \partial_{\mu\alpha} n^0(\mathbf{r}) \partial_{\alpha\nu} \quad (6)$$

where the groundstate kinetic stress tensor is $\bar{T}_{\mu\nu}^0 = \Re \sum_n f_n [\partial_\mu \psi_n(\mathbf{r})]^* [\partial_\nu \psi_n(\mathbf{r})] - \frac{\partial_{\mu\nu} n^0(\mathbf{r})}{4}$ [16].

In the absence of an external potential, equation (3) has time-periodic eigen-solutions defined by the hydrodynamic eigen-equation

$$-\Omega_N^2 n^0(\mathbf{r}) u_{N\mu}(\mathbf{r}) = [n^0(\mathbf{r}) \Phi_{\mu\nu}^0 + \hat{K}_{\mu\nu}] u_{N\nu}(\mathbf{r}) \quad (7)$$

where $\mathbf{u}_N(\mathbf{r}, t) = e^{i\Omega_N t} \mathbf{u}_N(\mathbf{r})$ is related to an eigenfunction of $\hat{\chi}_0$, Ω_N is related to the excitation energies (exactly in one- e^- systems) and $\int d\mathbf{r} n^0(\mathbf{r}) \mathbf{u}_N^*(\mathbf{r}) \cdot \mathbf{u}_M(\mathbf{r}) = \delta_{NM}$.

By definition $\chi_0(\mathbf{r}, \mathbf{r}'; \omega)$ is the change in density $n^1(\mathbf{r}) e^{i\omega t}$ in response to a small change in the KS potential of form $V^1(\mathbf{r}; \mathbf{r}', t) = \delta(\mathbf{r} - \mathbf{r}') e^{i\omega t}$ and can be obtained through equations (2)-(3). Expanding χ_0 in the eigen-solutions of (7) provides the convenient form

$$\chi_0(\mathbf{r}, \mathbf{r}'; \omega) = - \sum_N f_N(\omega) d_N(\mathbf{r}) d_N^*(\mathbf{r}') \quad (8)$$

where $f_N(\omega) = (\Omega_N^2 - \omega^2)^{-1}$ and $d_N(\mathbf{r}) = -\nabla \cdot [n^0(\mathbf{r}) \mathbf{u}_N(\mathbf{r})]$.

From (8) the projection of \hat{A} [see (1)] in reciprocal space is $A(\mathbf{q}, \mathbf{q}') = -\sum_N f_N(\omega) w_N^*(\mathbf{q}) w_N(\mathbf{q}')$ where

$$w_N(\mathbf{q}) = -i\mathbf{q} \sqrt{v(\mathbf{q})} \cdot \int d\mathbf{r} e^{i\mathbf{q} \cdot \mathbf{r}} n^0(\mathbf{r}) \mathbf{u}_N(\mathbf{r}) \quad (9)$$

or $w_N = \sqrt{v(\mathbf{q})} d_N(\mathbf{q})$ (here $v(\mathbf{q}) = 4\pi q^{-2}$). Setting $W_{NM} = \int \frac{d\mathbf{q}}{(2\pi)^3} w_N^*(\mathbf{q}) w_M(\mathbf{q})$ allows us to define an $N_{\text{Eig}} \times N_{\text{Eig}}$ matrix $\mathbb{A}(\omega)$ with elements $A_{NM}(\omega) = -f_N(\omega) W_{NM}$ and its Hermitian counterpart $\mathbb{B}(\omega)$ with

$$B_{NM}(\omega) = -\sqrt{f_N(\omega) f_M(\omega)} W_{NM}. \quad (10)$$

As $N_{\text{Eig}} \rightarrow \infty$ $\text{Tr}_N[F(\mathbb{B}(\omega))] = \text{Tr}_N[F(\mathbb{A}(\omega))] = \text{Tr}_{\mathbf{q}}[F(\hat{A}(\omega))]$ [17] for any analytic function F .

Defining the eigen-values of $\mathbb{B}(\omega)$ to be $\beta_\kappa(\omega)$ we reduce the correlation energy (1) to the form

$$E_c^{\text{CM}} = - \int_0^\infty \frac{d\sigma}{2\pi} \sum_\kappa \{\log[1 - \beta_\kappa(i\sigma)] + \beta_\kappa(i\sigma)\} \quad (11)$$

where we integrate over imaginary frequencies such that $f_N(i\sigma) = (\Omega_N^2 + \sigma^2)^{-1}$. In practice we need only a small number N_{Eig} of eigen-solutions for converged correlation energies and this calculation is $O(N_\sigma N_{\text{Eig}}^3)$.

In the Homogeneous Electron Gas (HEG) the TTGV method gives the exact $\hat{\chi}_0$ for $q \rightarrow 0$ and $\omega \rightarrow \infty$ and is robust for wavenumber $q \lesssim k_F$ and frequency $\omega \gtrsim v_F q$ where k_F/v_F is the Fermi wavenumber/velocity. This suggests that, as a crude first approximation, we should use the dRPA only for long-range correlation and use a local approximation for the short-range. A well-studied means of doing so is range-separation and is described in various papers[18]. It involves replacing the Coulomb potential by a long-range component only so that $v^{(\mu)}(r) = \text{erf}(\mu r) r^{-1}$ and $v^{(\mu)}(q) = 4\pi q^{-2} e^{-q^2/(4\mu^2)}$. This is equivalent to replacing (9) by $w_N^{(\mu)}(\mathbf{q}) = w_N(\mathbf{q}) e^{-q^2/(8\mu^2)}$. We label the corresponding correlation energy $E_c^{\text{lrCM}(\mu)}$. This has the additional benefit of improving convergence and speeding up calculation.

For $\hat{\chi}_0$ to be reliably approximated by continuum mechanics without a separate treatment of the low frequencies we must choose μ to be *substantially* less than k_F .

Here we use $\mu = 0.25 r_s^{-1} = 0.13 k_F$ where r_s is a global measure of the inter-electron distance. For the jellium slab problems studied below we simply choose r_s corresponding to the background charge density of each slab, though more general prescriptions exist.

The remaining correlation must be included from local approximations. We set

$$E_c^{\text{CM}(\mu)}[n] = E_c^{\text{lrCM}(\mu)} + \int d\mathbf{r} n(\mathbf{r}) \epsilon_c^{\text{Lsr}(\mu)} \quad (12)$$

where $\epsilon_c^{\text{Lsr}(\mu)}$ is the correlation energy per electron of the HEG with a short-ranged interaction, taken from[19].

The full dRPA exchange-correlation energy of a Kohn-Sham system is given by $E_{\text{xc}}[n] = E_x^{\text{EXX}} + E_c^{\text{dRPA}}$ where the exact exchange energy can be written explicitly as $E_x^{\text{EXX}} = -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' |\mathbf{r} - \mathbf{r}'|^{-1} |\sum_i f_i \psi_i^*(\mathbf{r}) \psi_i(\mathbf{r}')|^2$. Ideally we should also implement a range-separation for exchange, but this proves numerically difficult for the slab geometries we investigate. We instead use the ratio of the long-range exchange to total exchange of an HEG $A_x \approx 1.1 \mu r_s / \sqrt{1 + (1.1 \mu r_s)^2}$ as a prefactor for EXX and make up the remainder with the LDA. Combining this with (12) gives

$$E_{\text{xc}} = A_x E_x^{\text{EXX}} + (1 - A_x) E_x^{\text{LDA}} + E_c^{\text{CM}(\mu)}. \quad (13)$$

With $\mu r_s = 0.25$ we find $A_x = 0.265$.

The most trying calculation in this functional is that of equation (7) as \hat{K} is a spatially-dependent, differential operator. To overcome this problem we use an auxiliary basis set $\mathcal{B} \equiv \{\phi_j(\mathbf{r})\}_{j=1}^{N_{\text{Bas}}}$ which need not be mutually orthogonal but must be complete in the limit $N_{\text{Bas}} \rightarrow \infty$. \mathcal{B} can be optimised for a given geometry or problem. With this basis set we define our eigen-function to be $u_{N\mu}(\mathbf{r}) = \sum_j a_{N\mu}^j \phi_j(\mathbf{r})$ which we substitute into equation (7). This provides a set of $3N_{\text{Bas}} \times 3N_{\text{Bas}}$ coupled equations

$$\Omega_N^2 N_{jk}^0 a_{N\mu}^k = \{P_{jk\mu\nu}^0 + K_{jk\mu\nu}\} a_{N\nu}^k \quad (14)$$

while $N_{jk}^0 (a_{N\mu}^{j*} a_{M\mu}^k) = \delta_{NM}$ sets the orthogonality.

The non-operator terms in these equations are $N_{jk}^0 = \int d\mathbf{r} n^0(\mathbf{r}) \phi_j^*(\mathbf{r}) \phi_k(\mathbf{r})$ and $P_{jk\mu\nu}^0 = -\int d\mathbf{r} [n^0(\mathbf{r}) \partial_{\mu\nu} V^{\text{KS}}(\mathbf{r})] \phi_j^*(\mathbf{r}) \phi_k(\mathbf{r})$. Separating the final term into $K_{jk\mu\nu} = \int d\mathbf{r} \phi_j^*(\mathbf{r}) \hat{K}_{\mu\nu}(\mathbf{r}) \phi_k(\mathbf{r}) = K_{jk\mu\nu}^{(T)} - \frac{1}{4} K_{jk\mu\nu}^{(n)}$ and using integration by parts[20] gives

$$K_{jk\mu\nu}^{(T)} = - \int \{ \bar{T}_{\mu\alpha}^0 [\partial_\nu \phi_j^*] [\partial_\alpha \phi_k] + \bar{T}_{\alpha\nu}^0 [\partial_\alpha \phi_j^*] [\partial_\mu \phi_k] + \bar{T}_{\mu\nu}^0 [\nabla \phi_j^*] \cdot [\nabla \phi_k] \} d\mathbf{r} \quad (15)$$

$$K_{jk\mu\nu}^{(n)} = \int n^0 [\partial_\mu \nabla \phi_j^*] \cdot [\partial_\nu \nabla \phi_k] d\mathbf{r} \quad (16)$$

where all terms are functions of \mathbf{r} and all derivatives can be performed analytically on the basis functions.

As a test of our proposed functional we choose a two-slab metal problem with a background charge $n^+(z) = \rho[H(\frac{s}{2} - |z - L|) + H(\frac{s}{2} - |z + L|)]$ where $L = \frac{(D+s)}{2}$ and $H(x) = 1\forall(x \geq 0), 0$ otherwise. This defines two jellium slabs of width s , surface-to-surface distance D and background charge per unit area $\rho = 3/(4\pi r_s^3)$. The total number of electrons per unit area is set to $N_s = 2s\rho = \int_{-\infty}^{\infty} n^+(z)$.

The partial isotropy means $V^{\text{KS}}(\mathbf{r}) \equiv V^{\text{KS}}(z)$ and the KS wavefunctions take the form $\psi_{n\mathbf{k}_{\parallel}}(\mathbf{r}) = p_n(z)e^{-i\mathbf{k}_{\parallel} \cdot \mathbf{r}_{\parallel}}$ where $\int dz p_n^* p_m = (2\pi)^{-2} \delta_{nm}$. The KS energies are $\epsilon_{n\mathbf{k}_{\parallel}} = \epsilon_{n0} + \frac{1}{2}|\mathbf{k}_{\parallel}|^2$ with occupation $f_n = 2 \max(\epsilon_F - \epsilon_{n0}, 0)$. The density is thus $n^0(z) = \sum_n f_n |p_n(z)|^2$ and the kinetic pressure tensor is $\bar{\mathbf{T}}^0(z) = t^{0\parallel}(z)[\hat{x} \otimes \hat{x} + \hat{y} \otimes \hat{y}] + t^{0z}(z)\hat{z} \otimes \hat{z}$ with $t^{0\parallel}(z) = \sum_n f_n \frac{\epsilon_F - \epsilon_{n0}}{2} |p_n(z)|^2$ and $t^{0z}(z) = \sum_n f_n |\partial_z p_n(z)|^2 - \frac{1}{4} \partial_{zz} n^0(z)$.

For the present slab problem we choose auxiliary basis functions of the form $\phi_k(\mathbf{r}) = b_k(z)e^{-i\mathbf{q}_{\parallel} \cdot \mathbf{r}_{\parallel}}$ and set $\mathbf{u}_{N\mathbf{q}_{\parallel}} = \sum_k \phi_k(\mathbf{r})[a_{Nz}^k(q_{\parallel})\hat{z} + a_{N\parallel}^k(q_{\parallel})\hat{\mathbf{q}}_{\parallel}]$ (the $\hat{\mathbf{q}}_{\perp} = \mathbf{q}_{\parallel} \times \hat{z}$ term does not contribute to the correlation energy). Thus the eigen-equations are

$$\Omega_N^2(q_{\parallel})N_{jk}^0 a_{N\parallel}^k(q_{\parallel}) = K_{jk\parallel\parallel}(q_{\parallel})a_{N\parallel}^k(q_{\parallel}) + K_{jk\parallel z}(q_{\parallel})a_{Nz}^k(q_{\parallel}) \quad (17)$$

$$\Omega_N^2(q_{\parallel})N_{jk}^0 a_{Nz}^k(q_{\parallel}) = [P_{jkzz}^0 + K_{jkzz}(q_{\parallel})]a_{Nz}^k(q_{\parallel}) + K_{jkz\parallel}(q_{\parallel})a_{N\parallel}^k(q_{\parallel}) \quad (18)$$

which must be solved for each q_{\parallel} . Normalisation gives $\sum_{jk} N_{jk}^0 [a_{N\parallel}^{j*} a_{M\parallel}^k + a_{Nz}^{j*} a_{Mz}^k] = (2\pi)^{-2} \delta_{NM}$. Here N_{jk} and P_{jkzz}^0 are independent of q_{\parallel} while K_{jkzz} , $K_{jkz\parallel} = K_{kj\parallel z}^*$ and $K_{jk\parallel\parallel}$ are second, third and fourth order in iq_{\parallel} . They appear in full in the supplementary material.

Finally in this basis $w_{N\mathbf{q}_{\parallel}} = iv^{1/2}(\sqrt{q_{\parallel}^2 + q_z^2}) \int dz e^{iq_z z} n^0[q_{\parallel} u_{N\mathbf{q}_{\parallel}} + q_z u_{N\mathbf{q}_{\parallel} z}]$, $W_{NM}(q_{\parallel}) = -\int \frac{dq_z}{2\pi} w_{Nq_z}^* w_{Mq_z}$ and $E_c^{\text{lrCM}(\mu)} = -\int \frac{d\sigma}{2\pi} \int \frac{2\pi q_{\parallel} dq_{\parallel}}{(2\pi)^2} \text{Tr}[L(\mathbb{B}(q_{\parallel}, i\sigma))]$ with B_{NM} from (10) and $L(x) = \log(1-x) + x$.

We test our method on slab pairs with $s = 3a_0$, $r_s = 1.25a_0$ and $s = 5a_0$, $r_s = 2.07a_0$ which have been studied in ref. 21 and ref. 14 and 22 respectively. Especially in

	Tok(μ)	LDA	dRPA
$r_s = 1.25$ and $s = 3$, $\mu = 0.2$			
D_0	3.33	3.38	3.32‡
ϵ_b	0.74	0.53	0.79‡
C_{zz}	0.51	0.45	0.55‡
$r_s = 2.07$ and $s = 5$, $\mu = 0.12$			
D_0	1.57	1.56	1.62±0.1§
ϵ_b	1.78	1.72	1.85±0.1§
C_{zz}	1.31	1.38	1.32±0.1§

TABLE I. Energies are in mHa/ e^- and distance are in Bohr radii. ‡ from Ref. 21, § is guessed from Ref. 14 and 22 taking into account likely numerical errors.

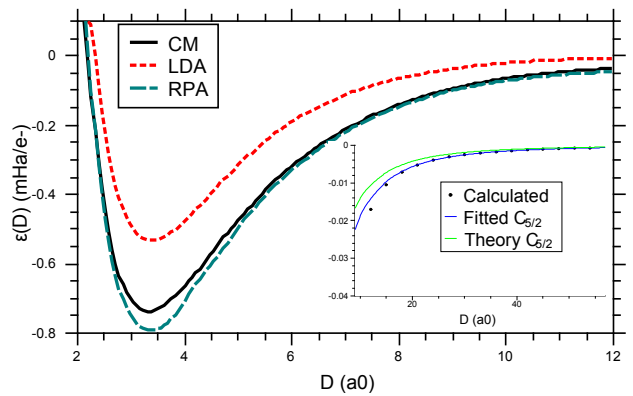


FIG. 1. $\bar{\epsilon}(D)$ graph for $r_s = 1.25$, $s = 3$. RPA data from [21]. Inset data shows the vdW dominated region.

the first case the LDA and dRPA give significantly different energy curves. We consider the cleavage energy per electron $\bar{\epsilon}(D) = \epsilon(D) - \epsilon(\infty) = [E_0(D) - E_0(\infty)]/N_s$ as a function of D . Slabs with $r_s < 4$ have a defined binding length D_0 where the force is zero. Thus a binding energy $\epsilon_b = |\bar{\epsilon}(D_0)|$ and an elastic modulus $C_{zz} = \partial_{DD} \bar{\epsilon}(D_0)$ can also be defined.

In Figure 1 we plot $\bar{\epsilon}(D)$ versus D for $r_s = 1.25$, $s = 3$. Our method matches the RPA closely for this system. Binding properties for both studied systems are tabulated in Table I and show that the $r_s = 2.07$, $s = 5$ system is less well-predicted but still much better than the LDA. If instead we set $\mu = \infty$ the results become much worse for both cases.

For widely separated slabs ($D \gg s$) the TTGV theory correctly describes coupled two-dimensional plasmons and hence correctly predicts the known asymptotic dRPA form[6] $\bar{\epsilon}(D \gg s) \approx -C_{5/2}(D+s)^{-5/2}$ where $C_{5/2} = 0.012562\sqrt{N_s}$ and $D+s$ is the distance between the centers of the slabs. With $s = 12.8a_0$ and $r_s = 2a_0 \dots 6a_0$ we calculate numerical solutions within 8% of the theory for $r_s = 2$ decreasing to just 2% error for $r_s = 6$. By contrast most other efficient vdW functionals would predict an incorrect power law exponent in this limit with $\bar{\epsilon}(D) \approx -C_4 D^{-4}$.

Calculations are quite efficient with the slowest step being either $O(N_r N_{\text{Bas}}^2)$, $O(27N_{\text{Bas}}^3)$ or $O(N_\sigma N_{\text{Eig}}^3)$. With highly non-optimised parameters[23] our code takes approximately eight times longer than the groundstate LDA calculation. Better optimisation could improve this result.

While results for our test systems are not perfect, they show closer agreement with the dRPA than the LDA both in the binding region and for larger D . The vdW dispersive physics is treated accurately and shows excellent agreement with the dRPA in contrast to other methods. The current prescription has a wide scope for refinement both empirically through adjustment of μ and A_x and by introducing better physics, most obviously through

improved treatment of low-frequency behaviour.

Overall we believe this method shows promise as an *efficient* functional with correct long-range correlation. Its ability to correctly predict the vdW physics of metallic systems is a distinct advantage over other efficient vdW functionals. It is very likely that this advantage would carry over into more typical systems with unusual geometries.

The authors would like to thank J. Jung, A. Savin, J. Àngyàn, I. Tokatly, and G. Vignale for fruitful discussions.

* Email: t.gould@griffith.edu.au

- [1] See page 1898 of R. H. French, V. A. Parsegian, R. Podgornik, R. F. Rajter, A. Jagota, J. Luo, D. Asthagiri, M. K. Chaudhury, Y.-m. Chiang, S. Granick, S. Kalinin, M. Kardar, R. Kjellander, D. C. Langreth, J. Lewis, S. Lustig, D. Wesolowski, J. S. Wettlaufer, W.-Y. Ching, M. Finnis, F. Houlihan, O. A. von Lilienfeld, C. J. van Oss, and T. Zemb, *Rev. Mod. Phys.* **82**, 1887 (2010).
- [2] J. Harl and G. Kresse, *Phys. Rev. B* **77**, 045136 (2008); *Phys. Rev. Lett.* **103**, 056401 (2009).
- [3] S. Lebègue, J. Harl, T. Gould, J. G. Àngyàn, G. Kresse, and J. F. Dobson, *Phys. Rev. Lett.* **105**, 196401 (2010).
- [4] H. Eshuis, J. Yarkony, and F. Furche, *J. Chem. Phys.* **132**, 234114 (2010); H. Eshuis and F. Furche, *J. Phys. Chem. Lett.* **2**, 983 (2011).
- [5] H.-Y. Kim, J. O. Sofo, D. Velegol, M. W. Cole, and A. A. Lucas, *J. Chem. Phys.* **124**, 074504 (2006); M. W. Cole, D. Velegol, H.-Y. Kim, and A. A. Lucas, *Mol. Sim.* **35**, 849 (2009).
- [6] B. E. Sernelius and P. Björk, *Phys. Rev. B* **57**, 6592 (1998); J. F. Dobson, A. White, and A. Rubio, *Phys. Rev. Lett.* **96**, 073201 (2006); T. Gould, K. Simpkins, and J. F. Dobson, *Phys. Rev. B* **77**, 165134 (2008); T. Gould, E. Gray, and J. F. Dobson, *Phys. Rev. B* **79**, 113402 (2009).
- [7] N. D. Drummond and R. J. Needs, *Phys. Rev. Lett.* **99**, 166401 (2007).
- [8] D. Lu, Y. Li, D. Rocca, and G. Galli, *Phys. Rev. Lett.* **102**, 206411 (2009); H.-V. Nguyen and S. de Gironcoli, *Phys. Rev. B* **79**, 205114 (2009).
- [9] We adopt the following notations: s is a scalar, \mathbf{v} is a 3D vector, \mathbb{T} is a 3x3 tensor and \mathbb{M} is a general matrix. Operators wear a hat \hat{o} and repeated indices are summed over. Hartree atomic units with $\hbar = e^2/(4\pi\epsilon_0) = m = 1$ are used throughout.
- [10] S. Grimme, *J. Comp. Chem.* **27**, 1787 (2006); A. Tkatchenko and M. Scheffler, *Phys. Rev. Lett.* **102**, 073005 (2009); O. A. Vydrov and T. V. Voorhis, *Phys. Rev. Lett.* **103**, 063004 (2009).
- [11] M. Dion, H. Rydberg, E. Schröder, D. C. Langreth, and B. I. Lundqvist, *Phys. Rev. Lett.* **92**, 246401 (2004); H. Rydberg, B. I. Lundqvist, D. C. Langreth, and M. Dion, *Phys. Rev. B* **62**, 6997 (2000); H. Rydberg, M. Dion, N. Jacobsen, E. Schröder, P. Hyldgaard, S. I. Simak, D. C. Langreth, and B. I. Lundqvist, *Phys. Rev. Lett.* **91**, 126402 (2003); D. C. Langreth, M. Dion, H. Rydberg, E. Schröder, P. Hyldgaard, and B. I. Lundqvist, *Int. J. Quantum Chem.* **101**, 599 (2005).
- [12] I. V. Tokatly, *Phys. Rev. B* **75**, 125105 (2007).
- [13] J. Tao, X. Gao, G. Vignale, and I. V. Tokatly, *Phys. Rev. Lett.* **103**, 086401 (2009); X. Gao, J. Tao, G. Vignale, and I. V. Tokatly, *Phys. Rev. B* **81**, 195106 (2010).
- [14] J. F. Dobson and J. Wang, *Phys. Rev. Lett.* **82**, 2123 (1999).
- [15] J. F. Dobson, *Phys. Rev. Lett.* **73**, 2244 (1994).
- [16] We define the kinetic stress tensor $\bar{\mathbb{T}}^0$ slightly differently from Tao *et al* but \hat{K} is identical.
- [17] It can be shown that $\text{Tr}_N[\mathbb{B}^p] = \text{Tr}_q[\hat{A}^p]$ for any p . The general rule follows from the Taylor expansion of $F(x)$.
- [18] A. Savin and H.-J. Flad, *International Journal of Quantum Chemistry* **56**, 327 (1995); T. Leininger, H. Stoll, H.-J. Werner, and A. Savin, *Chem. Phys. Lett.* **275**, 151 (1997); I. C. Gerber and J. G. Àngyàn, *Chem. Phys. Lett.* **415**, 100 (2005).
- [19] J. Toulouse, A. Savin, and H.-J. Flad, *Int. J. Quantum Chem.* **100**, 1047 (2004).
- [20] We expand $\partial_{\mu\nu}\mathbf{a} \cdot \mathbf{b} = [\partial_{\mu\nu}\mathbf{a}] \cdot \mathbf{b} + [\partial_\mu\mathbf{a}] \cdot [\partial_\nu\mathbf{b}] + \mathbf{a} \leftrightarrow \mathbf{b}$ and match terms.
- [21] J. Jung, P. García-González, J. F. Dobson, and R. W. Godby, *Phys. Rev. B* **70**, 205107 (2004).
- [22] J. F. Dobson and J. Wang, *Phys. Rev. B* **69**, 235104 (2004).
- [23] For our calculations we utilise an overcomplete basis set of form $e^{i\frac{\pi n z}{s}}$ and $\tanh(k_t z)e^{i\frac{\pi n z}{s}}$ where k_t is selected for rapid convergence. Convergence is reached with $N_{\text{Bas}} = 42$, $N_{q_{\parallel}} = 55$, $N_{q_z} = 800$, $N_\sigma = 250$ and $N_{\text{Eig}} \leq 60$. Ground-state calculations have $N_z = 500 \dots 1000$.