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Efficient, long-range correlation from occupied wavefunctions only

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Via continuum mechanics [PRL 103,086401] with Random Phase Approximation (dRPA) screening, we develop a numerically efficient general-geometry electronic exchange-correlation energy functional. It gives correct asymptotic power laws for dispersion interactions between insulators or metals. As a numerical example we obtain the full binding energy curves $\bar{\epsilon}(D)$ for parallel metal slabs of small but finite thickness: at all separations D our $\bar{\epsilon}(D)$ agrees better with full dRPA correlation calculations than does the Local Density Approximation, while being much more efficient than full dRPA correlation.

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An increasing body of work¹⁻⁴ 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 materials² 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 coefficients⁵ and power laws⁶ 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 obtained through a standard groundstate approximation such as the LDA. This is typically the numerical bottleneck. Recent developments⁸ attempt to bypass unoccupied states but can encounter problems 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 via integration on the imaginary frequency axis through the Adiabatic Connection and Fluctuation Dissipation Theorem (ACFD) approach

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

where $\hat{A}(\omega) = -\hat{v}^{1/2} \hat{\chi}_0(\omega) \hat{v}^{1/2}$ is an Hermitian operator⁹.

Other efficient van der Waals (vdW) 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-empirically¹⁰ or derived¹¹ 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. Very large, anisotropic molecules and metallic and graphitic surface physics (e.g. binding of graphite on metal surfaces) are two classes of systems

where standard methods are inaccurate¹² and dRPA is difficult.¹³

Here we solve (1) accurately thus avoiding the pairwise additive approximation, but we use the continuum mechanics of Tokatly, Tao, Gao and Vignale¹⁴⁻¹⁶ to avoid expensive wavefunction-based evaluation of $\hat{\chi}_0$. Their linearized continuum mechanics (CM) scheme¹⁵ uses the continuum fluid displacement \mathbf{u} , which is related to the density perturbation n^1 by¹⁵⁻¹⁷ $n^1(\mathbf{r}, t) = -\partial_\mu [n^0(\mathbf{r}) u_\mu(\mathbf{r}, t)]$. For a small change to the Kohn-Sham (KS) potential $V^1(\mathbf{r}, t)$ CM theory approximates \mathbf{u} through the following hydrodynamic-like equation (from equations 3, 4 and 14-16 of [15])

$$\partial_{tt} u_\mu(\mathbf{r}, t) = \frac{-\Phi_{\mu\nu}^0 u_\nu(\mathbf{r}, t) + F_\mu^0(\mathbf{r}, t)}{n^0(\mathbf{r})} - \partial_\mu V^1(\mathbf{r}, t) \quad (2)$$

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

The force F_μ^0 is defined in equation 14 of [15]. Careful manipulation of equation 14 allows us to write it as $F_\mu^0 = -\hat{K}_{\mu\nu} u_\nu(\mathbf{r}, t)$. Here \hat{K} is a tensor, Hermitian ($\hat{K}_{\mu\nu} = \hat{K}_{\nu\mu}^\dagger$) operator defined by

$$\hat{K}_{\mu\nu} = \hat{K}_{\mu\nu}^{(T)} - \frac{1}{4} \hat{K}_{\mu\nu}^{(n)} \quad (3)$$

$$\hat{K}_{\mu\nu}^{(T)} = \partial_\alpha \bar{T}_{\mu\nu}^0 \partial_\alpha + \partial_\nu \bar{T}_{\mu\alpha}^0 \partial_\alpha + \partial_\alpha \bar{T}_{\alpha\nu}^0 \partial_\mu \quad (4)$$

$$\hat{K}_{\mu\nu}^{(n)} = \partial_{\nu\alpha} n^0(\mathbf{r}) \partial_{\alpha\mu}. \quad (5)$$

It involves the electron density and groundstate kinetic stress tensor¹⁸

$$\bar{T}_{\mu\nu}^0 = \Re \sum_i f_i [\partial_\mu \psi_i(\mathbf{r})]^* [\partial_\nu \psi_i(\mathbf{r})] - \frac{[\partial_{\mu\nu} n^0(\mathbf{r})]}{4} \quad (6)$$

where the sum is over occupied orbitals.

In the absence of an external potential, (2) has time-periodic eigen-solutions defined by the hydrodynamic eigen-equation

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

where N labels the sorted eigen-modes, $\Omega_N > \Omega_{N-1}$ is related to the KS excitation energies (exactly in

one-electron systems), $\mathbf{u}_N(\mathbf{r})$ is related to an eigenfunction of $\hat{\chi}_0$ and obeys the orthogonality condition $\int d\mathbf{r} n^0(\mathbf{r}) \mathbf{u}_N^*(\mathbf{r}) \cdot \mathbf{u}_M(\mathbf{r}) = \delta_{NM}$. The use of this eigen-equation is crucial to our efficient correlation functional.

By definition the tensor polarizability $X_{0\mu\nu}(\mathbf{r}, \mathbf{r}'; \omega)$ is the time-periodic response of the μ cartesian component of the polarization $-n^0(\mathbf{r})\mathbf{u}_N(\mathbf{r})$ to an external electric field in the ν direction, while χ_0 is the change in density $n^1(\mathbf{r})$ in response to a small change in the KS potential of form $V^1(\mathbf{r}; \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$. They can be obtained through (2), where expansion in the eigen-solutions of (7) provides the convenient forms

$$X_{0\mu\nu}(\mathbf{r}, \mathbf{r}', i\sigma) = \sum_N F_N(i\sigma) p_{N\mu}^*(\mathbf{r}) p_{N\nu}(\mathbf{r}') \quad (8)$$

$$\chi_0(\mathbf{r}, \mathbf{r}', i\sigma) = - \sum_N F_N(i\sigma) d_N^*(\mathbf{r}) d_N(\mathbf{r}'). \quad (9)$$

Here $F_N(i\sigma) = (\Omega_N^2 + \sigma^2)^{-1}$, $\mathbf{p}_N = n^0(\mathbf{r})\mathbf{u}_N(\mathbf{r})$ and the density-mode $d_N(\mathbf{r}) = [-\nabla \cdot \{n^0(\mathbf{r})\mathbf{u}_N(\mathbf{r})\}] = -[\nabla \cdot \mathbf{p}_N]$.

Using (9) we can write the operator \hat{A} appearing in the correlation energy (1) in separable form in reciprocal space, $A(\mathbf{q}, \mathbf{q}') = \sum_N \sqrt{v(q)} \{d_N^*(\mathbf{q}) F_N(\omega) d_N(\mathbf{q}') \sqrt{v(q')}\}$, where $v(q) = 4\pi q^{-2}$ for a pure Coulomb pair potential. This form avoids expensive Coulomb integrals. Evaluation of (1) in this N -basis is not quite trivial since $\{d_N\}$ are not orthonormal. However if we define an Hermitian matrix \mathbb{B} , related to \hat{A} , as follows (with B_{NM} , F_N and F_M evaluated at $\omega = i\sigma$)

$$B_{NM} = \sqrt{F_N F_M} \int \frac{d\mathbf{q}}{(2\pi)^3} v(q) d_N(\mathbf{q}) d_M^*(\mathbf{q}) \quad (10)$$

then we can show¹⁹ by induction on p that $\text{Tr}_N[\mathbb{B}^p] = \text{Tr}_q[\hat{A}^p]$. It follows that $\text{Tr}_N[G(\mathbb{B}(i\sigma))] = \text{Tr}_q[G(\hat{A}(i\sigma))]$ for any analytic function G . Considering the case $G(x) = \log(1+x) - x$ we immediately evaluate (1), using the eigenvalues $\{\beta_\kappa(i\sigma)\}$ of $\mathbb{B}(i\sigma)$, through

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

The correlation energy functional (10)-(11) is our main result, though in practice, as discussed below, we obtain the eigenvalues $\{\beta_\kappa\}$ via use of an additional basis and keep only a finite number N_{Eig} of them, and we also sometimes employ the functional within a range-separation technique. Note that (11) does not require explicit evaluation of $\hat{\chi}_0$.

In practice we seem only to need a small number N_{Eig} of eigen-solutions to converge correlation energies to a sufficiently small error ($\propto 1/\Omega_{N_{\text{Eig}}}^3$) within CM theory where the cutoff is equivalent to a maximum transition frequency $\Omega_{N_{\text{Eig}}}$. This agrees with other observations (e.g. ref. 8) that calculating E_c through a diagonalisation of $\hat{\chi}_0 \hat{v}$ requires few eigenvalues for convergence.

A similar approach can be employed for exact dRPA of molecules where the set of transition densities $d_{ia}(\mathbf{r}) =$

$\psi_i^*(\mathbf{r})\psi_a(\mathbf{r})$ (with orbital i occupied and a unoccupied) replace the set of d_N , while $B_{iai'a'}$ replaces B_{NM} . This similarity means that many techniques developed for the full dRPA, such as those of Ref. 4, and 20, can be adapted to work for the CM-dRPA. This approach is usually impractical in periodic bulk systems where the transitions must be calculated for each \mathbf{k} in the BZ such that we require $d_{iak}(\mathbf{q}) = \psi_i^*(\mathbf{r})\psi_{a\mathbf{k}+\mathbf{q}}(\mathbf{r})$ and $B_{iai'a'\mathbf{k}}$ replaces B_{NM} . Thus a calculation of this form has a prefactor of at least $O(N_{\mathbf{k}})$ where there are $N_{\mathbf{k}}$ points sampled in the BZ. If we assume that transitions within bands are typically of a similar magnitude to gaps between neighbouring bands, the CM-dRPA calculations will reduce the number of transitions by at least $O(N_{\mathbf{k}})$. Even assuming no further reductions, calculation of E_c is thus led by $O(N_{\text{Eig}} N_{\mathbf{k}})$ under the CM-dRPA and $O(N_{\text{Eig}} N_{\mathbf{k}}^2)$ for full dRPA where the extra $N_{\mathbf{k}}$ comes from the final integration over the BZ. A similar reduction should occur in molecular systems with more than three electrons.¹⁹

The most demanding calculation in this functional method is evaluation of equation (7), as \hat{K} is a spatially-dependent, differential operator. To overcome this problem we use an auxiliary basis set $\mathcal{B} \equiv \{\phi_j(\mathbf{r})\}$, of size N_{Bas} , which need not be mutually orthogonal but must be complete in the limit $N_{\text{Bas}} \rightarrow \infty$. Choice of this basis is the only part of this scheme that differs for different geometries or systems: for example, plane waves for periodic systems, gaussians for atoms and molecules. With a given basis set we expand our CM eigen-function (7) as $u_{N\mu}(\mathbf{r}) = \sum_j a_{N\mu}^j \phi_j(\mathbf{r})$ which we substitute into equation (7). This provides a set of $3N_{\text{Bas}} \times 3N_{\text{Bas}}$ coupled equations

$$-\Omega_N^2 N_{jk}^0 a_{N\mu}^k = \{\Phi_{jk\mu\nu}^0 + K_{jk\mu\nu}\} a_{N\nu}^k \quad (12)$$

while $a_{N\mu}^{j*} N_{jk}^0 a_{M\mu}^k = \delta_{NM}$ follows from 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 $\Phi_{jk\mu\nu}^0 = - \int d\mathbf{r} [n^0(\mathbf{r}) \partial_{\mu\nu} V^{\text{KS}}(\mathbf{r})] \phi_j^*(\mathbf{r}) \phi_k(\mathbf{r})$. 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 gives

$$K_{jk\mu\nu}^{(T)} = - \int \{ \bar{T}_{\mu\alpha}^0 [\partial_\nu \phi_j^*] [\partial_\alpha \phi_k] + \bar{T}_{\alpha\nu}^0 [\partial_\alpha \phi_j^*] [\partial_\mu \phi_k] + \bar{T}_{\mu\nu}^0 [\nabla \phi_j^*] \cdot [\nabla \phi_k] \} d\mathbf{r} \quad (13)$$

$$K_{jk\mu\nu}^{(n)} = \int n^0 [\partial_\nu \nabla \phi_j^*] \cdot [\partial_\mu \nabla \phi_k] d\mathbf{r} \quad (14)$$

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

Surprisingly for a hydrodynamic-style approach, CM theory gives the exact bare responses \mathbf{X}_0 , χ_0 to irrotational fields of one- and two($\uparrow\downarrow$)-electron systems around their groundstate.^{14,19} This means that our correlation scheme will give the same results as dRPA for the asymptotic vdW interaction between two hydrogen or two helium atoms.

To explore this further we use two exact sum rules relating CM to exact KS theory. They are derived explicitly from the f- and third-moment sum rules in Appendix E of Ref. [16]:

$$1 = \sum_{ja} h_{jaN}, \quad \Omega_N^2 = \sum_{ja} h_{jaN} \omega_{ja}^2. \quad (15)$$

Here $h_{jaN} = \frac{2|f_j - f_a| |K_{jaN}|^2}{|\omega_{ja}|}$ and N labels any chosen CM eigenmode, with Ω_N the CM eigen-frequency from (7) or (12). ω_{ja} is a KS eigen-energy difference of an occupied orbital $|j\rangle$ and unoccupied orbital $|a\rangle$ with Fermi occupation factors f_j and f_a . $K_{jaN} = \int \langle j | \hat{\mathbf{J}}(\mathbf{r}) | a \rangle \cdot \mathbf{u}_N(\mathbf{r}) d\mathbf{r}$ is an overlap integral of the CM modes displacement field \mathbf{u}_N and the KS transition current density, the latter defined as a matrix element of the Schrödinger current density operator $\hat{\mathbf{J}}(\mathbf{r})$. As a consequence of (15), $\Omega_N \geq \epsilon_L - \epsilon_H$ for isolated systems and, from Bloch symmetry, $\Omega_{N\mathbf{q}} \geq \min_{\mathbf{k}} (\epsilon_{L\mathbf{k}+\mathbf{q}} - \epsilon_{H\mathbf{k}})$ for periodic systems where L labels the lowest unoccupied orbital or band and H labels the highest occupied.

One implication of this is that a Kohn-Sham insulator will remain an insulator under CM, in the sense of finite responses (8)-(9) as $\sigma \rightarrow 0$. Thus¹⁹ CM theory obeys the well-known vdW laws for insulators with (e.g.) a $-C_4 D^{-4}$ asymptotic binding for two thin layers. This is a very strong feature of the CM theory, not shared by common approximated ACFD theories^{11,21} where explicit cutoffs have to be imposed in the tails in order to suppress metallic-like response.

In the opposite limit of a homogeneous electron gas (HEG), CM is analytically soluble, agrees with the true χ_0 for $q \ll k_F$, $\omega \gg v_F q$, and in particular has a “metallic” infinite polarizability, $\chi_0 \rightarrow \infty$ as q and $\omega \rightarrow 0$. Electron-gas-like (metallic) systems nevertheless pose a difficult test for CM theory because the single-particle-like excitations occurring for $\omega < v_F q$, (and thus not accurately described by CM), can make significant contributions to the RPA correlations, mainly at short spatial range (large ~~wavelength~~ **wavenumber**).

This inaccuracy can be improved in metallic systems by employing a further approximation to avoid the greatest inaccuracies. We introduce range-separation (RS) such that the short-range physics is treated by a local scheme. This makes *no contribution* to vdW asymptotic physics. A well-studied RS scheme is described in various papers.²² It involves choosing a q_{RS} and splitting up the Coulomb potential, with a long-range component $v^{(q_{RS})}(r) = \text{erf}(q_{RS}r)r^{-1}$, equivalent to replacing $v(q) = 4\pi/q^2$ by $v^{(q_{RS})}(q) = 4\pi e^{-q^2/(4q_{RS}^2)}/q^2$ in (10). We label the corresponding correlation energy $E_c^{\text{lrCM}(q_{RS})}$. This has the additional benefit of accelerating convergence, a feature shared with full dRPA calculations utilizing RS.

For $\hat{\chi}_0$ to be reliably approximated by continuum mechanics without a separate treatment of the low frequencies we must choose q_{RS} to be *substantially* less than k_F . Here we use $q_{RS} = 0.25r_s^{-1} = 0.13k_F$ where r_s is a global

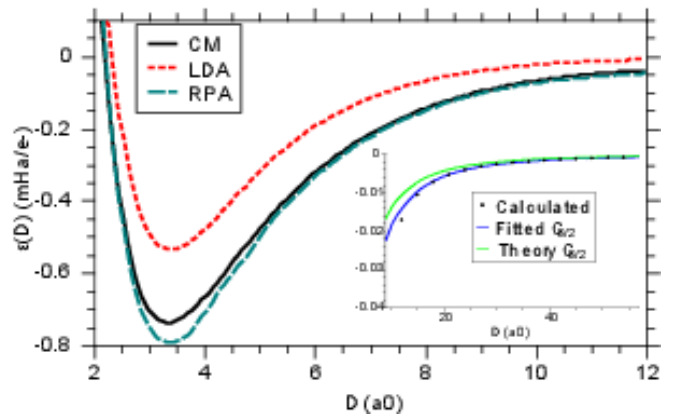


FIG. 1. $\bar{\epsilon}(D)$ graph for $r_s = 1.25$, $s = 3$. RPA data from.²⁵ Inset data shows the vdW dominated region.

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 so that

$$E_c^{\text{CM}(q_{RS})}[n] = E_c^{\text{lrCM}(q_{RS})} + \int d\mathbf{r} n(\mathbf{r}) \epsilon_c^{\text{Lsr}(q_{RS})} \quad (16)$$

where $\epsilon_c^{\text{Lsr}(q_{RS})}$ is the correlation energy per electron of the HEG with a short-ranged interaction, taken from.²³

Ideally we must 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 $A_x \approx 1.1q_{RS}r_s/\sqrt{1+(1.1q_{RS}r_s)^2}$ as a prefactor for the exact exchange (EXX) $E_x^{\text{EXX}} = -\frac{1}{2} \int d\mathbf{r} d\mathbf{r}' |\mathbf{r} - \mathbf{r}'|^{-1} |\sum_n f_n \psi_n^*(\mathbf{r}) \psi_n(\mathbf{r}')|^2$ and make up the remainder with the LDA. Combining this with (11) gives $E_{xc} = A_x E_x^{\text{EXX}} + (1 - A_x) E_x^{\text{LDA}} + E_c^{\text{CM}(q_{RS})}$.

As a numerical test of our proposed functional we choose the difficult case of two thin metal slabs described in Refs. 21, 24, and 25. This system is defined by three parameters only: the width of the slabs s , the inner surface-surface distance D and the positive background charge electron density $\rho = 3/(4\pi r_s^3)$. The total number of electrons per unit area is $N_s = 2s\rho = \int_{-\infty}^{\infty} n^+(z) dz$.

	CM	LDA	dRPA	CM	LDA	dRPA
	$r_s = 1.25, s = 3$			$r_s = 2.07, s = 5$		
D_0	3.33	3.38	3.32‡	1.57	1.56	1.62±0.1§
ϵ_b	0.74	0.53	0.79‡	1.78	1.72	1.85±0.1§
C_{zz}	0.51	0.45	0.55‡	1.31	1.38	1.32±0.1§

TABLE I. Groundstate properties of two slab systems under different approximations. Energies are in mHa/e⁻ and distance are in Bohr radii. ‡ from Ref. 25, § is guessed from Refs. 21 and 24 taking into account estimated error bars.

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. 25 and Refs. 21 and 24 respectively. Especially in 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 $q_{RS} = \infty$ the results become much worse for both cases. For widely separated slabs ($D \gg s$) the CM theory correctly and analytically describes coupled two-dimensional plasmons and hence correctly predicts the known asymptotic dRPA form⁶ $\bar{\epsilon}(D \gg s) \approx -0.012562\sqrt{N_s}(D+s)^{-5/2}$. With $s = 12.8a_0$ and $r_s = 2a_0 \dots 6a_0$ we calculate $C_{5/2}$ numerically within 8% of the theory. By contrast most other efficient vdW functionals would predict an incorrect power law exponent in this limit with $\bar{\epsilon}(D) \approx -C_4D^{-4}$.

Further calculation showed that a 10% change in range parameter q_{RS} changed the binding energy by only about 1% and the minimum of the graph is shifted somewhat up and to the left or down and to the right. Theory and preliminary tests also suggest that range separation will be less important in finite systems or bulk insulators than it is for metals, although the efficiency gains may still make it useful.

In our CM calculations pn parallel jellia we use auxiliary¹⁹ basis functions $\phi_{k\mathbf{q}_{\parallel}}(\mathbf{r}) = b_k(z)e^{-i\mathbf{q}_{\parallel}\cdot\mathbf{r}_{\parallel}}$ at $N_{q_{\parallel}} \mathbf{q}_{\parallel}$ points. All calculations are quite efficient with the slowest step being evaluation of W_{NM} at $O(N_{q_{\parallel}}N_{q_z}N_{\text{Bas}}^2)$. Convergence is reached with $N_{\text{Bas}} = 42$, $N_{q_{\parallel}} = 55$, $N_{\sigma} = 250$ and $N_{\text{Eig}} \leq 60$. Our dRPA calculation takes approximately eight times longer than the groundstate LDA calculation. Test runs of full RPA calculations for these systems took hours, compared to minutes for our functional, consistent with $N_{q_{\parallel}} = 55$.

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 , with a marked improvement in speed over full dRPA. 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 q_{RS} and the exchange

functional and by introducing better physics, most obviously through improved (semi-local) treatment of low-frequency behaviour which will reduce dependence on the range separation.

Furthermore preliminary tests suggest that metals are a worst-case for CM theory - i.e. that range separation will be much less needed for bound and insulating systems.

In summary, we have derived and developed a new efficient general-geometry energy functional with correct long-ranged correlation behavior. It is implemented as follows. (i) We take as inputs the groundstate density n^0 and stress tensor $\bar{\mathbf{T}}^0$ [through (6)] obtained from the *occupied* orbitals of a prior groundstate calculation (e.g. LDA or GGA). We feed n^0 and $\bar{\mathbf{T}}^0$ into our new compact form of the linear CM equations [equations (3)-(5)]. These describe the linear response of the electronic fluid displacement $\mathbf{u}(\mathbf{r})\exp(-i\omega t)$ to small perturbations. (ii) We project these equations onto an auxiliary basis set spanning typical fluid displacements for the geometry at hand. Within this basis, standard linear algebra [equation (12), equivalent to (7)] provides a set of fluid displacement eigenvectors \mathbf{u}_N and eigen-frequencies Ω_N . These describe self-sustaining motions of the independent-electron fluid in the presence of the groundstate Kohn-Sham potential. (iii) We evaluate the dRPA correlation energy (1) directly, without first assembling the bare responses (8)-(9). We do this by using $\{\mathbf{u}_N, \Omega_N\}$ to construct a matrix \mathbb{B} [through (10)], related to the dRPA screening operator $\chi_0\hat{v}$. Its eigenvalues $\{\beta_{\kappa}\}$ give the dRPA correlation energy from (11).

Our functional can predict correctly the vdW physics of metallic (see figure 1) and insulating systems [see below (15)]. This is a distinct advantage over other *efficient* vdW functionals. It is currently being implemented for periodic systems, which should enable meaningful energy calculations for (e.g.) vdW bonded nanosystems such as metallic nanotube arrays or graphene on metals in non-ideal geometries. These systems require non-pair-additive high-level computations (e.g. dRPA) with a large unit cell, which is beyond present computational power.

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- ⁹ We adopt the following notations: s is a scalar, \mathbf{v} is a 3D vector, \mathbf{T} is a 3x3 tensor and \mathbb{M} is a general matrix. Operators wear a hat \hat{o} . Hartree atomic units with $\hbar = e^2/(4\pi\epsilon_0) = m = 1$ are used throughout. Greek subscripts represent cartesian components and are summed over if repeated. Derivatives ∂_α and ∇ act on *everything* to the right except in square brackets.
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