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Insights into the spurious long-range nature of local r_s -dependent non-local exchange-correlation kernels

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A systematic route to go beyond the exact exchange plus random phase approximation (EXX/RPA) is to include a physical exchange-correlation kernel in the adiabatic-connection fluctuation-dissipation theorem. In the previous study [J. Chem. Phys. 140, 18A520 (2014)], we found that non-local kernels with a screening length depending on the local Wigner-Seitz radius, $r_s(\mathbf{r})$, suffer an error associated with a spurious long-range repulsion in van der Waals bounded systems, which deteriorates the binding energy curve as compared to RPA. We analyze the source of the error and propose to replace $r_s(\mathbf{r})$ by a global, average r_s in the kernel. Exemplary studies with the Corradini, del Sole, Onida, and Palumbo (CDOP) kernel show that while this change does not affect the already outstanding performance in crystalline solids, using an average r_s significantly reduces the spurious long-range tail in the exchange-correlation kernel in van der Waals bounded systems. When this method is combined with further corrections using local dielectric response theory, the binding energy of the Kr dimer is improved three times as compared to RPA.

Keywords: van der Waals dispersion, RPA correlation energy, long-range correlation, exchange-correlation kernel, local dielectric response theory

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I. INTRODUCTION

Advances in *ab initio* electronic structure methods, in particular density functional theory (DFT), have made them the standard tool to obtain quantitative structural and electronic information for a wide range of materials^{1,2}. Despite the success of DFT in describing materials with strong chemical bonds, standard DFT functionals under the local density (LDA) or generalized gradient approximation (GGA) and hybrid functionals fail to capture the van der Waals (vdW) dispersion interaction originated from long-range correlation effects³. The lack of vdW dispersion forces limits the predictive power of DFT in many important systems, such as molecular crystals⁴⁻⁶, layered materials⁷⁻⁹, and organic-inorganic interfaces¹⁰⁻¹².

As part of the electronic correlation energy, the dispersion energy can be evaluated from wavefunction-based methods, e.g. coupled cluster theory or quantum Monte Carlo (QMC), but at substantial computational cost. An alternative strategy is to incorporate dispersion interactions into the DFT framework, and extensive efforts had been made in the past two decades along this direction. These proposals include the empirical pairwise potential method¹³⁻¹⁶, the Tkatchenko-Scheffler method that employs density-dependent C_6 coefficients^{17,18}, and different flavors of vdW density functionals¹⁹⁻²⁴ that contain non-local correlation energy terms up to the second order. Recently, the adiabatic-connection fluctuation-dissipation theorem (ACFDT)²⁵⁻²⁷ has attracted considerable attention, because of its *ab initio* nature combined with a moderate computational cost^{4,28,29}.

The exchange correlation energy in ACFDT can be written as a sum of the exact exchange (EXX) and correlation energy (E_c) expressed in terms of response functions^{25,27},

$$E_c = -\frac{1}{2\pi} \int_0^1 d\lambda \int_0^\infty d\omega \text{Tr} \left\{ v(\mathbf{r}, \mathbf{r}') \left[\chi^\lambda(\mathbf{r}, \mathbf{r}', i\omega) - \chi_0(\mathbf{r}, \mathbf{r}', i\omega) \right] \right\}, \quad (1)$$

where χ and χ_0 are the screened and bare dielectric response functions, and $v(\mathbf{r}, \mathbf{r}') = \frac{1}{|\mathbf{r}-\mathbf{r}'|}$ is the Coulomb kernel. The frequency integration is performed along the imaginary axis, and λ is the coupling constant. Here integration over dummy variables is implied in the product of operators. Formally, χ^λ can be obtained from Dyson's equation as $\chi^\lambda = \chi_0 + \chi_0 (\lambda v + f_{xc}^\lambda) \chi^\lambda$, where f_{xc}^λ is the exchange-correlation kernel. Under the random phase approximation (RPA), f_{xc}^λ is neglected, and Eq. 1 is simplified to

$$E_c^{RPA} = \frac{1}{2\pi} \int_0^\infty d\omega \text{Tr} \left\{ \log[\epsilon_{RPA}(i\omega)] + v \chi_0(i\omega) \right\}, \quad (2)$$

where $\epsilon_{RPA} = 1 - v \chi_0$. In practice, E_c^{RPA} can be computed from the eigenvalues of ϵ_{RPA} .

The EXX/RPA method corrects the self-interaction error³⁰ and captures the vdW interactions at both intermediate and long ranges^{31,32}. Besides the correct long-range asymptotic behavior, the RPA correlation energy includes non-additive dispersion energy (e.g. the Axilrod-Teller-Muto three-body term) up to an infinite order³³. As a fifth-rung DFT method, EXX/RPA provides a balanced description of strong (e.g., covalent bonds) and weak (e.g., vdW dispersion forces) chemical bonds, and systematic improvement over LDA and GGA has been demonstrated in the lattice constant and bulk modulus in crystalline solids, the binding energy in rare gas dimers and weakly bounded molecular complexes in the S22 set, the molecule adsorption energy on the surface, and reaction barrier heights^{31,32,34,35}.

Despite its overall good performance, EXX/RPA is known to underbind both small molecules and crystals^{30,34,35}. This problem is also known as “the RPA atomization energy puzzle”³⁶. On average, the EXX/RPA atomization energy underbinds solids compared to experiment by about 0.69 eV and molecules by about 0.45 eV³⁵. In weakly interacting systems, the same trend persists. Toulouse *et al.*³⁷ found that the equilibrium binding energies of rare gas dimers are underestimated by 0.4 meV in the He dimer and by 6.8 meV in the heavier Kr dimer. Similarly, the cohesive energy of noble gas crystals is underestimated by 5 ~ 10 meV³⁸. For the S22 dataset, EXX/RPA underbinds by 16%^{31,39,40}. The cohesive energy of molecular crystals is underestimated several tens of meV^{4,41}. The underbinding in RPA is the consequence of neglecting f_{xc} in the Dyson’s equation, resulting in a large error in the short-range correlation energy⁴². To go beyond RPA in the ACFDT framework, a proper f_{xc} needs to be restored that satisfies known physical constraints.

Since the exact form of f_{xc} is unknown, different models of f_{xc} have been proposed. Dobson and Wang⁴³ proposed an “energy-optimized” local and static kernel. Gould⁴⁴ constructed a radial exchange hole kernel to approximate the true exchange kernel via a weighted radial averaging. Ruzsinszky and co-workers⁴⁵ introduced a short-ranged, exchange-like kernel that is one-electron self-correlation free and exact for two-electron systems in the high-density limit. On the other hand, very promising results were obtained from a class of kernels that depend on the Wigner-Seitz radius (r_s) of the local electron density, $f_{xc}(r_s, \mathbf{r} - \mathbf{r}')$, which we refer to as local r_s -dependent non-local kernels⁴⁶⁻⁵¹. One example is the renormalized adiabatic local density approximation (rALDA) or its Perdew-Burke-Ernzerhof variant (rAPBE), which truncates the ALDA or APBE kernel at a cutoff wave vector⁴⁶⁻⁵⁰. An alternative approach is to generalize $f_{xc}(r_s, q)$ derived from the homogeneous electron gas (HEG)

model^{49,51}. Among many available choices^{52–57}, the static kernel introduced by Corradini, del Sole, Onida, and Palumbo (CDOP)⁵⁴ is particularly appealing, as it is a simple numerical fit of the accurate QMC data of the HEG model at different r_s ⁵⁸. Consequently, the CDOP kernel satisfies the correct small and large q asymptotic power law behaviors at the static limit.

For the HEG model, both the rALDA (rAPBE) kernel and the CDOP kernel eliminate the error in the absolute RPA correlation energy, and yield good agreement with the QMC results^{46,51}. In addition, the CDOP pair distribution function corrects the unphysical behavior of RPA near the origin⁵¹. For inhomogeneous systems, the CDOP kernel significantly improves the absolute correlation energy over RPA for bulk silicon^{49,51}, and the resulting correlation energy is in excellent agreement with the value from diffusion Monte Carlo (DMC)⁵⁹. The rALDA kernel gives a significantly better description of the short-range correlations for covalent bonds compared to RPA and yields a fourfold improvement over RPA binding energies in both molecules and solids⁴⁶. The rAPBE kernel yields nearly twofold improvement in the formation energy over RPA across a wide range of metal oxides⁵⁰.

Although local r_s -dependent non-local kernels are remarkably successful in improving the absolute correlation energy and fixing “the RPA atomization energy puzzle” in covalent bonded systems, they failed to solve the RPA underbinding problem in vdW bounded systems. Surprisingly, the situation becomes even worse. The rALDA binding energy of bilayer graphene is 3 meV less than RPA⁴⁷. Similarly, the rAPBE graphene-Ni(111) binding curve becomes less attractive than RPA⁴⁸. Finally, in rare gas dimers, the CDOP binding energy is about 3 meV less than RPA⁵¹ for the Kr dimer. Detailed analysis of the Kr dimer suggests that this underbinding problem in vdW systems results from a spurious long-range tail intrinsic to local r_s -dependent non-local kernels⁵¹. To make beyond-RPA methods in ACFDT widely applicable and accurate, this issue has to be carefully addressed.

The rest of the paper is organized as the following. In the Theory and Method section, we first show that the effect of a local kernel is to increase the binding energy in vdW systems; then following Ref. 51, we use the CDOP kernel as an example to investigate the spurious long-range interaction in non-local terms; next we propose to replace the local r_s by an average r_s to reduce the spurious long-range interaction, which we refer to as aCDOP; finally we outline the idea to further reduce the spurious long-range interaction in vdW systems by applying the local dielectric response theory⁶⁰, which we refer to as

aCDOP_{loc}. In the Results and Discussions section, we evaluate aCDOP under two limits. Bulk silicon represents crystalline solids close to the HEG limit, and the Kr dimer represents inhomogeneous systems of a strong vdW character. The performance of aCDOP_{loc} is tested using the Kr dimer.

II. THEORY AND METHOD

A. Effect of a local exchange-correlation kernel

Patrick and Thygesen⁴⁹ pointed out a close connection between ACFDT and the range-separated Kohn-Sham (KS) theory^{37,61–63}. Given a static and linear kernel, $f_{xc}^\lambda(q) = \lambda f_{xc}(q)$, E_c in ACFDT can be partitioned into two contributions, $E_c = E_c^{LR} + E_c^{SR}$, where⁴⁹

$$E_c^{LR} = \frac{1}{2\pi} \int_0^\infty d\omega \operatorname{Tr} \{ \ln [1 - v_{eff} \chi_0(i\omega)] + v_{eff} \chi_0(i\omega) \}, \quad (3)$$

$$E_c^{SR} = \frac{1}{2\pi} \int_0^\infty d\omega \operatorname{Tr} \{ f_{xc} [\chi^\lambda(i\omega) - \chi_0(i\omega)] \}. \quad (4)$$

The expression of E_c^{LR} is similar to Eq. 2, except that v is replaced by the effective interaction, $v_{eff} = v + f_{xc}$. Like ϵ_{RPA} , one can define $\epsilon_{eff} = 1 - v_{eff} \chi_0$. When applied to the Constantin and Pitarke (CP) kernel⁵⁶, v_{eff} has the same expression as in the range-separated RPA⁶¹, $v_{eff} = \operatorname{erf}(\mu R)/R$. The range-separation parameter, $\mu = k_F \approx 1.92/r_s$, is typically between 0.4 and 1.2^{61–63} with k_F being the Fermi wave vector.

Now let us focus on E_c^{LR} in a simple scenario of a homonuclear rare gas dimer at the non-interacting limit, where the electron densities of the two atoms (A and B) do not overlap. For simplicity, we consider a one-band model, i.e., one eigenmode of ϵ_{eff} per atom. The frequency dependence is dropped in the derivation, because the conclusion is frequency independent. Define the eigenmode of each atom as ϕ_A and ϕ_B , and the on-site and coupling elements as

$$\langle \phi_A | \epsilon_{eff} | \phi_A \rangle = \langle \phi_B | \epsilon_{eff} | \phi_B \rangle = \epsilon_0, \quad (5)$$

$$\langle \phi_A | \epsilon_{eff} | \phi_B \rangle = \langle \phi_B | \epsilon_{eff} | \phi_A \rangle^* = t, \quad (6)$$

where ϵ_0 is positive and $\eta \equiv |t|/\epsilon_0 < 1$. The one-band model is a good approximation in the weak-coupling regime where $\eta \ll 1$ or when the effect of the vdW dispersion is dominated by one eigenmode. The eigenvalues of the dimer is $\epsilon_\pm = \epsilon_0 \pm t$. It is reasonable to assume

that the overlap between ϕ_A and ϕ_B is negligible. The interaction energy of the dimer is given by

$$\Delta E_c^{LR} \propto \ln(\epsilon_+) + \ln(\epsilon_-) - 2\ln(\epsilon_0) = \ln(1 - \eta^2). \quad (7)$$

Note that terms with linear dependence on the eigenvalues cancel completely. Apparently, ΔE_c^{LR} is negative, as one expects from the vdW attraction. Because both v and $-\chi_0$ are positive definite, and a local f_{xc} is typically negative definite⁴³, ϵ_0 decreases at the presence of a local f_{xc} as compared to RPA. Since ϕ_A and ϕ_B do not overlap, a local f_{xc} does not affect t . As a result, η increases. Because ΔE_c^{LR} is a monotonically decreasing function of η , a local f_{xc} makes the vdW attraction stronger than RPA. The derivation above does not require f_{xc} to be a Dirac delta function. As far as f_{xc} is spatially localized, i.e., $\langle \phi_A | f_{xc} | \phi_B \rangle$ vanishes, the same arguments still hold.

B. Spurious long-range nature of the local r_s -dependent CDOP kernel

In the HEG model, f_{xc} is expressed in terms of the local field factor, G , through $f_{xc} = -vG$. The CDOP kernel⁵⁴ is static, and it is a numerical fit to the QMC $G(q)$ of the HEG model⁵⁸,

$$G^{CDOP}(q) = CQ^2 + \frac{BQ^2}{g + Q^2} + \alpha Q^4 e^{-\beta Q^2}, \quad (8)$$

where $Q \equiv q/k_F$. The parameters C , B , g , α and β are functions of r_s . $G^{CDOP}(q)$ satisfies the physical constraints at long and short wavelength limit, known as the acoustic sum rule and the cusp condition⁶⁴. Its real space expression,

$$f_{xc}^{CDOP}(\mathbf{r}) = -\frac{4\pi C}{k_F^2} \delta(\mathbf{r}) - B \frac{e^{-\sqrt{g}k_F r}}{r} + \frac{\alpha k_F}{4\pi^2 \beta} \left(\frac{\pi}{\beta}\right)^{3/2} \left[\frac{k_F^2 r^2}{2\beta} - 3\right] e^{-k_F^2 r^2 / 4\beta}, \quad (9)$$

consists of three terms: a delta function, a Yukawa potential, and a Gaussian potential. Both the Yukawa and Gaussian potentials are non-local and depend on r_s .

Generally speaking, there is no unique procedure to generalize a model $f_{xc}(r_s, q, \omega)$ of HEG to inhomogeneous electronic systems, which has a general form of $f_{xc}(\mathbf{r}, \mathbf{r}', \omega)$ in the real space or $\tilde{f}_{xc}^{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega)$ in the reciprocal space. The latter can be obtained from the real space expression through a double Fourier transformation⁴⁹,

$$\tilde{f}_{xc}^{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega) = \frac{1}{V} \int_V d\mathbf{r} \int_V d\mathbf{r}' e^{-i(\mathbf{q} + \mathbf{G}) \cdot \mathbf{r}} f_{xc}(\mathbf{r}, \mathbf{r}', \omega) e^{i(\mathbf{q} + \mathbf{G}') \cdot \mathbf{r}'}, \quad (10)$$

where V is the volume of the whole crystal. An intuitive and practical step forward is to symmetrize non-symmetric (NS) kernels that evaluate r_s at $\mathbf{r}$ and $\mathbf{r}'$ separately^{49,51},

$$f_{xc}(\mathbf{r}, \mathbf{r}', \omega) = \frac{1}{2} \left[f_{xc}^{NS}(r_s(\mathbf{r}), \mathbf{r} - \mathbf{r}', \omega) + f_{xc}^{NS}(r_s(\mathbf{r}'), \mathbf{r}' - \mathbf{r}, \omega) \right], \quad (11)$$

$$f_{xc}^{NS}(r_s(\mathbf{r}), \mathbf{r} - \mathbf{r}', \omega) = \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{\mathbf{G}} \tilde{f}_{xc}^{NS}(r_s(\mathbf{r}), q + G, \omega) e^{i(\mathbf{q} + \mathbf{G}) \cdot (\mathbf{r} - \mathbf{r}')}. \quad (12)$$

CDOP results presented in this work were obtained from this kernel symmetrization scheme, while density-^{47,65} and wavevector-based^{49,57} symmetrization schemes have also been proposed.

A common practice of different symmetrization schemes is a local approximation of r_s , which replaces the constant r_s in the HEG model by $r_s(\mathbf{r})$ evaluated from local electron density, $n(\mathbf{r})$. Although this local approximation of r_s is plausible for crystalline solids, it breaks down for vdW bounded systems, such as rare gas dimers. Because the decay lengths of the Yukawa and Gaussian potentials in the CDOP kernel are proportional to r_s , at very low electron density regions, the decay length becomes very large. As a result, the Yukawa and Gaussian potentials become delocalized, which create a spurious long-range repulsion that partially cancels the long range vdW attraction. In the Kr dimer case, we found that while the delta function in the CDOP kernel increases the binding energy as compared to RPA, which is consistent with the analysis of the one-band model, the Yukawa and Gaussian terms do the opposite⁵¹. This spurious long-range tail of the non-local kernel is the exact reason that makes the overall CDOP binding curve more repulsive than RPA in the Kr dimer.

Our calculations of the Kr dimer showed that the spurious long-range tail can be reduced by using a fixed global r_s or imposing an upper limit for the local r_s ⁵¹. These observations motivate us to employ a global, average r_s in aCDOP to avoid the artifact from low density regions. This procedure can be readily applied to other r_s -dependent non-local kernels. As discussed previously, aCDOP is conceptually very similar to range-separated RPA, with the equivalent range-separation parameter determined from first principle calculations.

C. Average r_s from the participation ratio

In bulk crystals, the average volume of an electron can be approximated by Ω/N_e , where Ω is the unit cell volume and N_e is number of electrons per unit cell. However, this procedure

can not be applied to finite systems, since the unit cell volume is no longer a well-defined physical quantity. Here we introduce a measure of the average volume based on the participation ratio (PR), which is applicable to both periodic and finite systems.

The concept of PR has been widely used in condensed matter physics to measure the degree of the (de)localization of an electronic orbital^{66,67} or the eigenvector of ϵ_{RPA} ⁶⁸. Consider an electron wavefunction (ψ_σ) evaluated on a uniform discrete lattice with N grid points, where σ denotes the electron spin. PR is defined as

$$PR = \frac{\left[\frac{1}{N} \sum_{i=1}^N |\psi_\sigma(\mathbf{r}_i)|^2\right]^2}{\frac{1}{N} \sum_{i=1}^N |\psi_\sigma(\mathbf{r}_i)|^4}. \quad (13)$$

At the limit of a localized electron, where $\psi_\sigma(\mathbf{r}_i) = \delta_{i,0}$, $PR = 1/N$. On the other hand, at the limit of a completely delocalized electron, where $|\psi_\sigma(\mathbf{r}_i)|^2 = 1/N$, $PR = 1$. Accordingly, for a given electron density of N_e electrons, $\rho(\mathbf{r})$, the effective unit cell volume, $\bar{\Omega}$, is given by

$$\bar{\Omega} = PR \times V_{cell} = \frac{\left[\int_{V_{cell}} \rho(\mathbf{r}) d\mathbf{r}\right]^2}{\int_{V_{cell}} \rho^2(\mathbf{r}) d\mathbf{r}}. \quad (14)$$

For bulk crystals, $V_{cell} = \Omega$. For finite systems, V_{cell} is the volume of the super cell. As far as $\rho(\mathbf{r})$ is fully converged with respect to V_{cell} , $\bar{\Omega}$ is well-defined. Therefore the average radius of an electron can be defined as

$$r_s^{PR} = \left(\frac{3\bar{\Omega}}{4\pi N_e}\right)^{1/3}. \quad (15)$$

D. Local dielectric response functions

We follow the same procedure in Ref. 51 to calculate E_c in aCDOP, which involves the calculation of matrix elements $\langle \delta\rho_i(i\omega) | f_{xc}^\lambda | \delta\rho_j(i\omega) \rangle$, where $\delta\rho_i$ is the i -th eigenmode of the charge density response of the whole system. It is convenient to partition the density response onto local orbitals to quantify the degree of the locality of the kernel. For example, in the case of rare gas dimers, it is useful to divide $\delta\rho$ into $\delta\rho^A$ and $\delta\rho^B$ localized on each atom. Such a partition is not straightforward, as the physical definition of local response functions is often ambiguous.

A formal solution to this problem is given by the local dielectric response theory⁶⁰, where the density response is expressed in the Wannier representation,

$$\Delta\rho = \frac{4}{\Omega} \sum_{\mathbf{R}n} |\Delta W_{\mathbf{R}n}\rangle \langle W_{\mathbf{R}n}|. \quad (16)$$

$\Delta W_{\mathbf{R}n}$ is the first order perturbation of the Wannier orbital, $W_{\mathbf{R}n}$, where $\mathbf{R}$ is the lattice vector, and n is the index of the Wannier function. $\Delta W_{\mathbf{R}n}$ can be solved from the generalized Sternheimer equation⁶⁰. Once the flavor of the Wannier function is chosen, the partition, $\delta\rho = \sum_{\mathbf{R}n} \delta\rho_{\mathbf{R}n}$, is exact. Therefore one can rigorously define $\delta\rho$ of subsystems as $\delta\rho^A = \sum_{\mathbf{R},n \in A} \delta\rho_{\mathbf{R}n}$ and $\delta\rho^B = \sum_{\mathbf{R},n \in B} \delta\rho_{\mathbf{R}n}$. In aCDOP_{loc}, we force the interatomic coupling to be zero, i.e., $\langle \delta\rho_i^A(i\omega) | f_{xc}^\lambda | \delta\rho_j^B(i\omega) \rangle = \langle \delta\rho_i^B(i\omega) | f_{xc}^\lambda | \delta\rho_j^A(i\omega) \rangle = 0$, such that f_{xc} is restricted to be completely localized on each atom.

III. RESULTS AND DISCUSSIONS

In this section, ACFDT calculations were carried out for bulk silicon and the Kr dimer. The computational details were described in the previous study⁵¹. Local dielectric response functions in aCDOP_{loc} were computed in the maximally localized Wannier function^{69,70} representation.

A. Bulk silicon

r_s^{PR} of bulk silicon at different lattice constants (a_0) are compared with the Wigner-Seitz radii (r_s^{WS}) in Table I. In general, one expects r_s^{PR} to be smaller than r_s^{WS} , because interstitial regions with lower than average $\rho(\mathbf{r})$ are partially excluded from $\bar{\Omega}$. At $a_0 = 9.40$, r_s^{PR} is 10% smaller than r_s^{WS} . The difference becomes more significant at larger a_0 , as the volume of the interstitial region increases. At $a_0 = 10.60$, r_s^{PR} is 13% smaller than r_s^{WS} .

E_c obtained from different approximations are shown in Fig. 1, where the results of LDA, RPA and CDOP have been reported in the previous study⁵¹. The CDOP kernel is known to correct the large error in E_c^{RPA} , and reproduce the DMC result⁵⁹ at $a_0 = 10.26$ with an error of 6.5 mRy⁵¹. Using a projector-augmented wave (PAW) implementation, Patrick and Thygesen⁴⁹ conducted a more thorough study of absolute correlation energies of crystals, which showed general improvement over RPA from local r_s -dependent non-local kernels with closest agreement from CDOP, CP and rALDA. aCDOP(r_s^{WS}) tends to yield a much smaller $|E_c|$ than CDOP, which worsens the agreement with DMC. The deviation grows as a function of a_0 . This trend can be understood, as r_s^{WS} overestimates the average electron radius, and the error in r_s^{WS} increases as a function of a_0 . Because r_s^{PR} yields a

more accurate r_s than r_s^{WS} , aCDOP(r_s^{PR}) shows a close agreement with CDOP. In fact, at $a_0 = 10.26$, aCDOP(r_s^{PR}) agrees with DMC slightly better than CDOP, with an error of -1.7 mRy. The equilibrium lattice constant (10.13 Bohr) and bulk modulus (101.8 GPa) in aCDOP(r_s^{PR}) are almost the same as those in CDOP (10.13 Bohr and 100.9 GPa).

B. the Kr dimer

In finite systems, e.g. the Kr monomer and dimer, notations aCDOP and aCDOP(r_s^{PR}) mean the same. As shown at the inset of Fig. 2, r_s^{PR} of the Kr monomer is fully converged to 1.248 with respect to the super cell size, which confirms that the procedure to compute r_s^{PR} through Eqs. 13-15 is numerically stable. In the range of $3.86 < d < 5.03$, r_s^{PR} of the dimer is the same as that of the monomer. We define the interaction energy as $\Delta E = E_{dimer} - 2E_{monomer}$. At the equilibrium distance (d_0), the binding energy is defined as $E_b = -\Delta E(d_0)$.

In CCSD(T)⁷¹, $d_0 = 4.06$ Å and $E_b = 16.4$ meV. Under RPA, E_b is underestimated by 3.8 meV, and d_0 is slightly longer by 0.05 Å⁵¹. CDOP based on local r_s introduces a spurious repulsion interaction in the Kr dimer, which results in a more repulsive binding curve than RPA⁵¹. Consequently, CDOP has a substantial error in both E_b (6.5 meV) and d_0 (0.15 Å). The spurious repulsion is largely removed in aCDOP by replacing local r_s by r_s^{PR} . When compared with RPA, E_b in aCDOP is 0.7 meV larger with d_0 almost unchanged. Therefore, aCDOP slightly improves the binding curve as compared to RPA. An even better agreement with CCSD(T) is obtained in aCDOP_{loc}, where f_{xc} is restricted to be completely localized on each Kr atom. In this way, any residual interatomic coupling through f_{xc} is explicitly removed. aCDOP_{loc} yields a remarkably accurate binding energy curve near d_0 as compared to CCSD(T), with an error of 1.3 meV in E_b and of -0.03 Å in d_0 .

IV. CONCLUSION

In summary, we showed that an average r_s can be properly defined for both crystalline solids and finite systems based on the participation ratio. Using this concept, we proposed an average r_s -based model of non-local exchange-correlation kernels in the ACFDT framework. As demonstrated by proof-of-concept studies, while this method does not affect the

already outstanding performance of the kernel in crystalline solids, it significantly reduces the spurious long-range repulsion for rare gas dimer systems, a text book example of vdW bounded systems. When this method is combined with further corrections using local dielectric response theory, the binding energy of the Kr dimer yields a threefold improvement over RPA.

Conceptually, r_s^{PR} may be used to derive first principle values of the range-separation parameter, e.g., $\mu = 1.1$ for bulk silicon and $\mu = 1.5$ for the Kr atom, in the range-separated KS theory. On the computational side, as r_s^{PR} is a constant, f_{xc} consists of simple potentials, which avoids the double Fourier transformations required for local r_s -based kernels. Therefore, this method makes ACFDT computationally more tractable.

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TABLES AND FIGURES

TABLE I. Wigner-Seitz radius (r_s^{WS}) and the average radius of an electron calculated from the participation ratio (r_s^{PR}) using Eq. 15 for bulk silicon at different a_0 (Bohr).

a_0	9.40	9.80	10.00	10.20	10.26	10.40	10.60
r_s^{WS}	1.84	1.91	1.95	1.99	2.00	2.03	2.07
r_s^{PR}	1.65	1.70	1.72	1.75	1.75	1.77	1.79

TABLE II. Equilibrium distance, d_0 (Å), and binding energy, E_b (meV), of the Kr dimer. Results are obtained from the spline interpolation of data in Fig. 2 with a distance spacing of 0.001 Å.

	RPA ^a	CDOP ^a	aCDOP	aCDOP _{loc}	CCSD(T) ^b
d_0	4.11	4.21	4.12	4.03	4.06
E_b	12.6	9.9	13.3	15.2	16.4

^a Ref. 51.

^b Ref. 71.

FIG. 1. Correlation energy curve in bulk silicon.

FIG. 2. Binding energy curve of the Kr dimer. Inset shows the convergence of r_s^{PR} of the Kr monomer as a function of super cell size.