

Simulation of All-Order Density-Functional Perturbation Theory, Using the Second Order and the Strong-Correlation Limit

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To boost the accuracy of electronic structure calculations, the exchange-correlation energy may be constructed from the Kohn-Sham orbitals. A formally exact construction is the density-functional perturbation series, which appears to diverge for many real systems. We predict the radius of convergence and resum this series, using only exact exchange and second-order correlation plus explicit density functionals for the strong-interaction limit. Our new correlation functional, along with exact exchange, predicts atomization energies with competitive accuracy and without the usual error cancellation.

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Electronic structure calculations, especially those for large molecules or unit cells, are usually based upon Kohn-Sham (KS) density-functional theory [1]. In this theory, the ground-state density $\rho(\mathbf{r})$ and total energy $E[\rho]$ are constructed by solving self-consistent one-electron equations, and only the density dependence of the exchange-correlation energy $E_{xc}[\rho]$ must be approximated. The simple local density approximation is surprisingly good for periodic solids, and generalized gradient approximations (GGA's) [2] have made the theory useful for molecules. However, these limited-form explicit density functionals have reached a limit of accuracy where any improvement for some systems or properties must be bought by a worsening elsewhere. Greater accuracy is needed before the theory will be useful for, for instance, the prediction of reaction rates.

Progress has been achieved by *implicit* density functionals [3] that construct the exchange-correlation energy from the KS orbitals. For example, predicted atomization energies of molecules have been improved by meta-GGA's which make use of the orbital kinetic energy density [4], and by hybrids [5–7] which mix a fraction ($\sim 25\%$) of exact exchange with GGA exchange and correlation. Formally (but not practically), the problem is solved by the density-functional perturbation theory for $E_{xc}[\rho]$ by Görling and Levy [8], for which only the first-order (exact exchange) and second-order (GL2 correlation) terms have been evaluated explicitly from the occupied and unoccupied KS orbitals.

In this Letter, we propose a way to resum the density-functional perturbation expansion. Only the first- and second-order (weak interaction) terms are treated exactly; explicit density functionals are used for the opposite (strong-interaction) limit. Our interaction strength interpolation (ISI) for the adiabatic connection provides a density functional [Eq. (11) below] that is both (i) competitively accurate for atomization energies (Table I) and (ii) exact in the high-density or exchange-dominated limit. Possible benefits of exact exchange [9] include improvements in derivative discontinuities and a more accurate KS poten-

tial [10], essential for a correct description of linear and nonlinear polarizabilities of large systems [11,12] as well as time-dependent and excited-state phenomena [13]. ISI generalizes GL2 in the same sense that GGA generalizes the second-order gradient expansion. It suggests that, for many real systems, the density-functional perturbation expansion is being applied outside its radius of convergence, so that resummation is a necessity.

The exchange-correlation energy $E_{xc}[\rho]$ of an interacting electron system with ground-state density $\rho(\mathbf{r})$ is defined by $E[\rho] = T_s[\rho] + U[\rho] + \int d^3r \rho(\mathbf{r})v_{\text{ext}}(\mathbf{r}) + E_{xc}[\rho]$. The kinetic energy $T_s[\rho]$ of the noninteracting system with the same density ρ , the Hartree energy

TABLE I. Atomization energies ΔE of 18 molecules (in units of 1 kcal/mole = 0.0434 eV), in Görling-Levy second-order perturbation theory (GL2) [6], in our ISI resummation, and from experiment (as in Ref. [4]). α_c is the estimated radius of convergence for the GL perturbation expansion of ΔW_α . Also shown are the PC values for ΔW_∞ and $\Delta W'_\infty$ (in units of 1 hartree = 27.21 eV).

Mol.	ΔE^{GL2}	ΔE^{ISI}	ΔE^{expt}	α_c	$\Delta W_\infty^{\text{PC}}$	$-\Delta W'_\infty^{\text{PC}}$
H ₂	114	107.3	109.5	1.97	0.313	0.270
LiH	70	58.8	57.8	0.91	0.258	0.197
Li ₂	39	22.5	24.4	0.39	0.111	0.086
LiF	193	142.7	138.9	0.21	0.616	0.692
Be ₂	22	5.7	3.0	0.27	0.122	0.120
CH ₄	454	423.4	419.3	1.25	1.536	1.683
NH ₃	340	300.9	297.4	0.93	1.293	1.485
OH	128	108.6	106.4	0.69	0.473	0.570
H ₂ O	274	235.7	232.2	0.63	0.973	1.182
HF	173	143.7	140.8	0.42	0.551	0.705
B ₂	190	68.1	71.0	0.06	0.375	0.465
CN	335	188.1	178.5	0.14	0.806	1.089
CO	355	265.9	259.3	0.22	0.891	1.238
N ₂	342	234.6	228.5	0.27	0.942	1.290
NO	265	157.9	152.9	0.23	0.801	1.127
O ₂	230	123.6	120.5	0.18	0.689	1.003
O ₃	407	136.8	148.2	0.15	1.157	1.658
F ₂	134	34.0	38.5	0.16	0.384	0.551
m.a.e.	74	4.3	...			

$U[\rho] \equiv \frac{1}{2} \int d^3r \int d^3r' \rho(\mathbf{r})\rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$, and the external potential $v_{\text{ext}}(\mathbf{r})$ are treated exactly in KS theory. The accuracy of GGA, meta-GGA, and hybrid approximations $E_{\text{xc}}^{\text{app}}[\rho]$ to $E_{\text{xc}}[\rho]$ results from some cancellation of the error in the exchange part or high-density limit [14]:

$$E_x^{\text{app}}[\rho] \equiv \lim_{\lambda \rightarrow \infty} \frac{1}{\lambda} E_{\text{xc}}^{\text{app}}[\rho_\lambda] \quad (1)$$

[where $\rho_\lambda(\mathbf{r}) = \lambda^3 \rho(\lambda \mathbf{r})$ is a scaled density] by the corresponding error in the correlation part $E_c^{\text{app}}[\rho] \equiv E_{\text{xc}}^{\text{app}}[\rho] - E_x^{\text{app}}[\rho]$. The exact exchange energy $E_x[\rho]$ is known explicitly as a Fock integral of the KS orbitals [1]. Since these orbitals are always available in a KS calculation, $E_x[\rho]$ is easily evaluated. However, exact exchange is not compatible with standard density functionals for correlation: The combination leads to unrealistic atomization energies for molecules [9,15,16]. The exact exchange hole in a molecule has a long-range part which is canceled by the exact correlation hole but not by the approximate ones. In other words, standard forms of $E_c^{\text{app}}[\rho]$ capture only dynamic or short-range, not static or long-range, correlation.

Our present approach uses *all* of the information provided by exact exchange (and more), starting from Görling-Levy (GL) perturbation theory [8] where the correlation energy is expanded in a series,

$$E_{\text{xc}}[\rho] = E_x[\rho] + \sum_{n=2}^{\infty} E_c^{\text{GL}n}[\rho]. \quad (2)$$

GL perturbation theory is closely related to the more popular one by Møller and Plesset (MP). The terms $E_c^{\text{GL}n}[\rho]$ can be found explicitly. In contrast to $E_x[\rho]$, however, their numerical evaluation is expensive, since they involve not only the N occupied KS orbitals but also all the unoccupied ones. Moreover, the computational expense increases rapidly with the order n . The series (2) converges slowly, and for many systems it might not converge at all.

To uncover the likely mathematical reason for the divergence, we consider the coupling-constant integral or adiabatic connection [17,18],

$$E_{\text{xc}}[\rho] = \int_0^1 d\alpha W_\alpha[\rho], \quad (3)$$

an exact expression for $E_{\text{xc}}[\rho]$. The integrand is

$$W_\alpha[\rho] = \langle \Psi_\alpha[\rho] | \hat{V}_{ee} | \Psi_\alpha[\rho] \rangle - U[\rho], \quad (4)$$

where $\hat{V}_{ee} = \sum_{i<j} |\hat{\mathbf{r}}_i - \hat{\mathbf{r}}_j|^{-1}$ is the Coulomb-repulsion two-particle operator and $\Psi_\alpha[\rho]$ is the antisymmetric wave function that yields the given density ρ and minimizes the expectation value $\langle \hat{T} + \alpha \hat{V}_{ee} \rangle$, with the operator \hat{T} for the kinetic energy. In other words, $\Psi_\alpha[\rho]$ is a wave function where the electronic repulsion is scaled by a factor $\alpha \geq 0$. (We use atomic units: $\hbar = m = e^2 = 1$.)

The perturbation series (2) is closely related to the Taylor expansion of $W_\alpha[\rho]$ around $\alpha = 0$,

$$W_\alpha[\rho] = E_x[\rho] + \sum_{n=2}^{\infty} E_c^{\text{GL}n}[\rho] n \alpha^{n-1}. \quad (5)$$

As α increases from 0, the function W_α starts from $W_0 = E_x$, first decreasing linearly but asymptotically approaching a constant value $W_\infty \leq E_x$ as $\alpha \rightarrow \infty$ [19,20]:

$$W_\alpha[\rho] \rightarrow W_\infty[\rho] + W'_\infty[\rho] \alpha^{-1/2} \quad (\alpha \rightarrow \infty). \quad (6)$$

As we shall see, this behavior can give the expansion (5) a finite radius of convergence $\alpha_c < 1$, which via Eq. (3) makes the series (2) diverge.

In the strong-interaction limit $\alpha \rightarrow \infty$, the electronic positions become strictly correlated within the continuous density $\rho(\mathbf{r})$. Any accidental clustering of these positions is strictly suppressed. In the simple “point charge plus continuum” (PC) model [19,21] for this limit, a spherical unit cell of empty space surrounds each electron; the electron can be off center in the presence of a density gradient. This model provides accurate approximations [21] to $W_\infty[\rho] \leq E_x[\rho]$ and $W'_\infty[\rho] \geq 0$ in Eq. (6):

$$W_\infty^{\text{PC}}[\rho] = \int d^3r \left\{ A \rho(\mathbf{r})^{4/3} + B \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})^{4/3}} \right\}, \quad (7)$$

$$W'_\infty^{\text{PC}}[\rho] = \int d^3r \left\{ C \rho(\mathbf{r})^{3/2} + D \frac{|\nabla \rho(\mathbf{r})|^2}{\rho(\mathbf{r})^{7/6}} \right\}, \quad (8)$$

with the constants $A = -1.451$, $B = 5.317 \times 10^{-3}$, $C = 1.535$, and $D = -2.558 \times 10^{-2}$. The accuracy of these second-order gradient forms seems to follow from the short range [21] of the PC cell. Because of a severe self-correlation error absent in meta-GGA [4], the local density approximation ($B = D = 0$) and standard GGA's fail in this limit [21].

We truncate the divergent expansion (5) at linear order (GL2) and make the simplest-possible resummation:

$$W_\alpha^{\text{ISI}}[\rho] = W_\infty[\rho] + \frac{X[\rho]}{\sqrt{1 + Y[\rho]\alpha + Z[\rho]}} \quad (9)$$

(“interaction-strength interpolation”), where the coefficients are chosen so that both $E_x[\rho]$ and the $n = 2$ term of the expansion (5) as well as the asymptotic behavior (6) are reproduced correctly,

$$X = \frac{xy^2}{z^2}, \quad Y = \frac{x^2y^2}{z^4}, \quad Z = \frac{xy^2}{z^3} - 1, \quad (10)$$

with $x = -4E_c^{\text{GL}2}[\rho]$, $y = W'_\infty[\rho]$, and $z = E_x[\rho] - W_\infty[\rho]$. $W_\alpha^{\text{ISI}}[\rho]$ has all the fundamental properties of the unknown exact integrand $W_\alpha[\rho]$, as listed in Ref. [19]. We use the PC model for $W_\infty[\rho]$ and $W'_\infty[\rho]$.

By analytic integration [Eq. (3)] of the function (9), we obtain the ISI exchange-correlation functional,

$$E_{\text{xc}}^{\text{ISI}}[\rho] = W_\infty + \frac{2X}{Y} \left[(1 + Y)^{1/2} - 1 - Z \ln \left(\frac{(1 + Y)^{1/2} + Z}{1 + Z} \right) \right]. \quad (11)$$

Unlike the other accurate functionals $E_{xc}^{app}[\rho]$ available, the ISI functional has the *exact* exchange part, $E_x^{ISI}[\rho] \equiv E_x^{exact}[\rho]$. This follows from Eq. (1) via scaling relations given in Refs. [19] and [21]. Therefore, ISI does *not* depend upon a cancellation of errors between E_x and E_c .

Since evaluation of the GL2 energy is computationally rather expensive (as it is for the corresponding term in the more popular MP series), accurate values for $E_c^{GL2}[\rho]$ are usually unavailable in the literature. An exception arises [6] for molecular atomization energies,

$$\Delta E[\rho_{mol}, \{\rho_{at}^k\}] = \sum_{k=1}^K E[\rho_{at}^k] - E[\rho_{mol}], \quad (12)$$

which are energy *differences*. In Eq. (12), ρ_{mol} and the ρ_{at}^k ($k = 1, \dots, K$) are, respectively, the ground state densities of the molecule and its K separated atoms after atomization.

Utilizing frozen-core ideas along with GGA densities, orbitals, and exchange potentials, Ernzerhof [6] provided the *differences* $\Delta E_c^{GL2}[\rho_{mol}, \{\rho_{at}^k\}]$ but not the values $E_c^{GL2}[\rho]$ for the individual densities ρ_{at}^k and ρ_{mol} . Consequently, we cannot make the interpolation (9) for the individual integrands $W_\alpha[\rho]$. However, the weak- and strong-interaction limits are preserved when the same analytic form (9) is used to model the difference function $\Delta W_\alpha[\rho_{mol}, \{\rho_{at}^k\}] \equiv \sum_{k=1}^K W_\alpha[\rho_{at}^k] - W_\alpha[\rho_{mol}]$ which, after integration via Eq. (3), yields the contribution $\Delta E_{xc}[\rho_{mol}, \{\rho_{at}^k\}]$ to the quantity (12). Thus we have used in x , y , and z of Eq. (10) the *differences* ΔE_x and ΔE_c^{GL2} from the third and last columns of Table 2 in Ref. [6] and our ΔW_∞^{PC} and $\Delta W_\infty'^{PC}$, evaluated with GGA [2] densities at the same experimental geometries used in Ref. [6].

Table I shows our results for 18 molecules. The GL2 results from Ref. [6] (using $\Delta E_{xc}^{GL2} = \Delta E_x^{exact} + \Delta E_c^{GL2}$) display severe overbinding, especially for the multiply bonded molecules (the last eight in Table I, including the strong-static-correlation cases F_2 and O_3). Our ISI interpolation to the PC values of ΔW_∞ and $\Delta W_\infty'$, which represents a simple resummation of GL perturbation theory, greatly improves the accuracy of the predicted atomization energies, reducing the mean absolute error from 74.4 to 4.3 kcal/mole. This is achieved *without* error cancellation, since E_x^{ISI} is exact exchange. The meta-GGA of Ref. [4], which does rely upon error cancellation, makes a mean absolute error of 4.1 kcal/mole for these molecules.

The explicit expression for $E_c^{GL2}[\rho]$ is [8]

$$E_c^{GL2}[\rho] = - \sum_{\nu=1}^{\infty} \frac{|\langle \Psi_0 | \hat{V}_{ee} - \hat{V}_H - \hat{V}_x | \Psi_\nu \rangle|^2}{E_0^\nu - E_0}. \quad (13)$$

Here, Ψ_ν is the ν th excited state of the KS single-particle Hamiltonian \hat{H}_{KS} (with ground state Ψ_0), i.e., $\hat{H}_{KS}\Psi_\nu = E_0^\nu \Psi_\nu$; \hat{V}_H and \hat{V}_x , respectively, are the one-particle operators of the Hartree potential $v_H(\mathbf{r}) \equiv \int d^3r' \rho(\mathbf{r}')/|\mathbf{r} - \mathbf{r}'|$ and the exchange potential $v_x(\mathbf{r}) \equiv \delta E_x[\rho]/\delta \rho(\mathbf{r})$.

Because the KS orbitals in E_x and E_c^{GL2} are implicit functionals of the density $\rho(\mathbf{r})$, so is E_{xc}^{ISI} of Eq. (11). For

an ion of fixed electron number N in the limit of large nuclear charge, this functional correctly reduces to $E_x + E_c^{GL2}$ and so meets the challenge to density-functional theory presented almost 20 years ago [22]: Its correlation energy correctly saturates to a negative constant for some values of N (e.g., 10) and decreases linearly with nuclear charge for other values of N (e.g., 4). Even van der Waals forces can be described [23] if the functional $E_c^{GL2}[\rho]$ is employed.

Although GL and MP perturbation theories are computationally expensive, it is not proven whether either series is convergent. There are indications that the MP series diverges even for systems such as the neon atom [24] which, because of their large HOMO-LUMO gaps, should be good candidates for convergence.

For our model integrand (9), the Taylor expansion (5) has a finite radius of convergence, given by

$$\alpha_c[\rho] = \frac{1}{Y[\rho]} \equiv \frac{(E_x - W_\infty)^4}{16(E_c^{GL2} W_\infty')^2}, \quad (14)$$

since the continuation of the function $W_\alpha^{ISI}[\rho]$ into the complex plane is not analytic at $\alpha = -\alpha_c[\rho]$. Figure 1(a) shows the function W_α^{ISI} for an example where $\alpha_c = 0.812 < 1$. Also shown are the truncated expansions

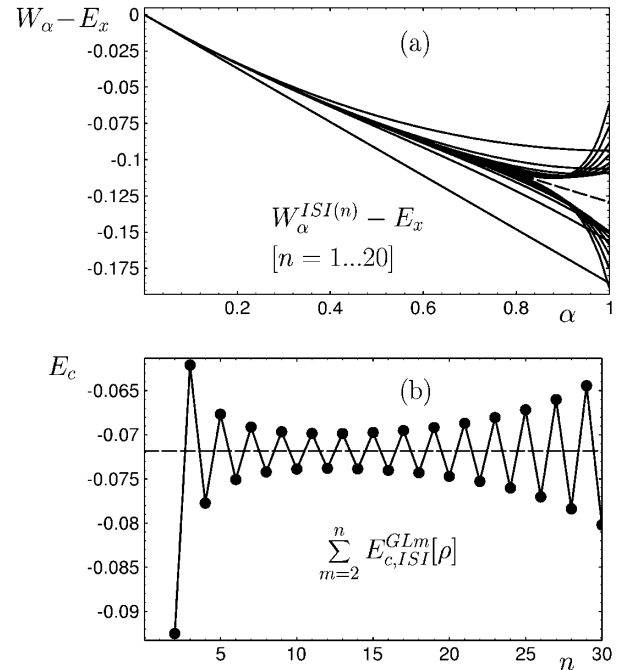


FIG. 1. (a) The model integrand W_α^{ISI} [Eq. (9)] in arbitrary units for a system with $E_x - W_\infty = 1.0$, $E_c^{GL2} = -0.0925$, and $W_\infty' = 3.0$ (dashed curve), and its truncated Taylor expansions of orders $n = 1-20$ (solid curves). The radius of convergence is $\alpha_c = 0.812$. (b) The corresponding integrated correlation energies $\sum_{m=2}^n E_{c,ISI}^{GLm}[\rho] = \int_0^1 d\alpha W_\alpha^{ISI(n)}$ in n th order Gorking-Levy perturbation theory (full circles) oscillate around $E_c^{ISI}[\rho]$ (horizontal dashed line) and eventually diverge. (An accurate truncation of the series would include only half of the smallest term, $m = 13$, and all of the lower-order terms.)

$W_\alpha^{\text{ISI}(n)} = \sum_{m=1}^n \frac{1}{m!} \alpha^m [d^m W_\alpha^{\text{ISI}} / d\alpha^m]_{\alpha=0}$ of this function for $n = 1-20$. Clearly, the series converges rapidly for $\alpha < \alpha_c$ but produces increasingly unphysical behavior for $\alpha > \alpha_c$. By integration, we can predict what we expect would be the outcome of GL perturbation theory, if carried to n th order. These correlation energies are plotted in Fig. 1(b) for $n = 2-30$. The oscillating pattern there results from the sign alternation of the coefficients in the divergent Taylor expansion of W_α^{ISI} , as can be seen in Fig. 1(a). These oscillations appear to be typical for a divergent perturbation expansion, carried to high orders n ; see Figs. 1 and 2 in Ref. [24].

In Table I, $\alpha_c \equiv \frac{1}{16}(\Delta E_x - \Delta W_\infty)^4 / (\Delta E_c^{\text{GL2}} \Delta W_\infty^2)$ is < 1 for many molecules, suggesting that the GL perturbation series for $E_c[\rho]$ does not converge in these cases. Since ΔW_α is the sum of the K functions $W_\alpha[\rho_{\text{at}}^k]$ and $-W_\alpha[\rho_{\text{mol}}]$, its radius of convergence α_c is the minimum of those for the individual functions of α , most likely that for $W_\alpha[\rho_{\text{mol}}]$. For some atoms (e.g., He, Be, and Ne), we find $1 < \alpha_c < 2$ [21].

While the specific radius of convergence (14) follows from our model (9), the physical reason for a finite radius of convergence could be an instability of $\Psi_\alpha[\rho]$ under mutual Coulomb attraction ($\alpha < 0$). According to Eq. (14), the radius of convergence α_c for the perturbation expansion is nonzero for any system in which E_c^{GL2} is finite. For the uniform electron gas on a per-electron basis, however, $E_c^{\text{GL2}} = -\infty$ and $\alpha_c = 0$; our Eqs. (9) and (11) remain finite, but are not accurate in this limit [21]. Generally, the random phase approximation provides a standard resummation for weak interactions which can be interpolated to the strong interaction limit or otherwise [25] corrected.

Although we have not done so, it is possible [3,9] to construct the exchange-correlation potential $\delta E_{\text{xc}}[\rho] / \delta \rho(\mathbf{r})$ for an implicit density functional.

Our analysis suggests that a perturbation expansion, even if divergent, contains strong information in its low-order terms. Additional independent information on the strong-interaction limit, which is simple [19–21] but not accessible by perturbation theory, can be used for an accurate resummation of the perturbation series.

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