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Exact-exchange time-dependent density-functional theory for static and dynamic polarizabilities

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Time-dependent density-functional theory (TDDFT) employing the exact-exchange functional has been formulated on the basis of the optimized-effective-potential (OEP) method of Talman and Shadwick for second-order molecular properties and implemented into a Gaussian-basis-set, trial-vector algorithm. The only approximation involved, apart from the lack of correlation effects and the use of Gaussian-type basis functions, was the consistent use of the adiabatic approximation in the exchange kernel and in the linear response function. The static and dynamic polarizabilities and their anisotropy predicted by the TDDFT with exact exchange (TDOEP) agree accurately with the corresponding values from time-dependent Hartree-Fock theory, the exact-exchange counterpart in the wave function theory. The TDOEP is free from the nonphysical asymptotic decay of the exchange potential of most conventional density functionals or from any other manifestations of the incomplete cancellation of the self-interaction energy. The systematic overestimation of the absolute values and dispersion of polarizabilities that plagues most conventional TDDFT cannot be seen in the TDOEP.

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I. INTRODUCTION

In spite of their remarkable success, Hohenberg-Kohn [1] and Kohn-Sham (KS) [2] density-functional theories (DFT's) have been criticized as not being a constructive theory, offering neither analytically nor numerically tractable a path to the exact exchange-correlation functional. However, this situation has changed dramatically in recent years when a number of rigorous theoretical approaches [3–22] to define converging approximations to the exact exchange-correlation functional have been proposed and have become subject to numerical scrutiny.

One such approach consists of the one-particle KS equation with a local, multiplicative exchange-correlation potential defined as the functional derivative of a nonlocal orbital-dependent exchange-correlation functional with respect to electron density [11,16,18–21]. The functionals are those established in *ab initio* wave function theory (WFT) such as many-body perturbation theory (MBPT) [11,16,18–20] and coupled-cluster (CC) [21] theory energy functionals. This approach therefore makes use of the variational theorem that is the centerpiece of KS DFT. Others include the Görling-Levy (GL) [8,9] and related [20–22] perturbation theories and the method of the Sham-Schlüter (SS) equation [5,7,10,12]. The GL perturbation theory invokes the premise that the exact one-electron KS orbitals must give rise to the electron density of the exact many-electron wave function. Accordingly, the GL perturbation theory insists that the electron density from the KS orbitals at a given order of the GL perturbation expansion of the exact exchange-correlation functional be correct through that order. In the SS method, a nonlocal self-energy operator in the Dyson equation is projected onto a local operator which is interpreted as the exchange-correlation potential in the KS equation. Collectively, these methods can be called *ab initio* DFT [20–23] in distinction to other conventional DFT's that embrace semiempiricism or nonsystematic approximations.

The essential features common to all *ab initio* DFT realizations are the use of systematic orbital-dependent exchange-correlation functionals and the locality ansatz of the corresponding exchange-correlation potentials. While much of the simplicity afforded by the conventional, non-orbital-dependent functionals may be lost in *ab initio* DFT, the latter provides a number of critical theoretical and practical advantages over the former. Principally, it gives an unambiguous theoretical route to the exact exchange-correlation functional. Second, it suggests a spectrum of new, useful methods as approximations to the exact exchange-correlation functional. Third, various analytical conditions and theorems that hold generally for KS DFT can be applied to the calculated quantities of *ab initio* DFT (e.g., Janak's theorem [24,25] for the ionization potential). While the locality ansatz has been introduced only to relate these methods to KS DFT, the local correlation potential embeds the correlation effects into orbitals and orbital energies and thereby can make the convergence of approximations in *ab initio* DFT potentially more rapid than the corresponding series in *ab initio* WFT [19–23] (cf. the use of natural [26] or Brueckner [27] orbitals in *ab initio* WFT). However, when carried through to the exact limit, *ab initio* DFT will be as expensive as the full configuration interaction method of *ab initio* WFT, in spite of the opposite assertion often made in favor of exact DFT.

While the different *ab initio* DFT methods may give rise

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to slightly different series of approximations to the exact exchange-correlation functional, they invariably derive just one exchange-only functional, which is the optimized-effective-potential (OEP) method introduced by Talman and Shadwick [28] (see also Ref. [29]). Being the exact exchange in *ab initio* DFT and the KS counterpart of the Hartree-Fock (HF) theory [30,31], the OEP shares many of the analytical features of the exact exchange-correlation potential [32]. The OEP has the correct $-1/r$ asymptotic behavior, cancels exactly the self-interaction, exhibits an integer derivative discontinuity [5,33,34], obeys the exchange virial theorem [35,36], satisfies the highest occupied molecular orbital (HOMO) condition (Janak's theorem), etc. The linear-combination-of-atomic-orbital (LCAO) algorithms of the OEP have been developed by Ivanov, Hirata, and Bartlett [37,38] and by Görling [39], which enabled rigorous exchange-only *ab initio* DFT calculations on an equal footing with the conventional Gaussian-basis-set DFT or *ab initio* WFT calculations. This has been extended to excited states via the time-dependent DFT formalism [40,41] within the adiabatic approximation (meaning the neglect of frequency dependence in the functional, in the potential, or in the kernel) and to electron correlation in the ground state via the second-order MBPT correlation functional [19–23].

In this article, as a part of the ongoing effort to establish the complete spectrum of *ab initio* DFT, we extend the LCAO algorithms of the OEP method to second-order responses to a frequency-dependent perturbation and assess the performance of the OEP for such properties. We derive the time-dependent density-functional theory (TDDFT) [42–49] employing the OEP (TDOEP) within the adiabatic approximation and apply that to static and dynamic polarizabilities, which are important properties determining the refractive index, Rayleigh scattering cross sections, Raman intensities, etc. In this article, the OEP and TDOEP should be understood to contain only the exchange component but no correlation effects. We adopt the algorithm that guarantees the correct $-1/r$ asymptotic decay of the OEP to ensure the quality of all orbitals which is vital to properties that probe virtual orbitals.

We will demonstrate that the TDOEP yields the identical results as a time-dependent HF (TDHF) theory for static and dynamic polarizabilities of (spin-unpolarized) two-electron systems and extremely close results for larger systems. This is congruous to the fact that the HF theory and OEP share the identical exchange energy functional, merely differing in the locality of the exchange potential in the latter, and to the expectation that the time dependence of the energies of these two methods should be similar (if not the same) in the adiabatic approximation. Within the limitation caused by the lack of electron correlation, the TDOEP is therefore as well behaved as the TDHF theory and does not suffer from the gross overestimation [46,50,51] of polarizabilities by conventional TDDFT caused by the wrong asymptotic behavior of exchange-correlation potentials [52,53] or from any other manifestation of the incomplete cancellation of the self-interaction error, which includes violation of the size extensivity [54] in excitation energies and the lack of charge-transfer separability [55]. Previously, Mori-Sánchez, Wu, and Yang [56] reported OEP polarizablity by the finite-differences method applying a small electric field to the molecules under study. Unlike this finite-differences method, our analytic approach is not limited to a static polarizability.

II. EXACT-EXCHANGE KS DFT

In the orthonormal, real, canonical KS orbital basis, the time-dependent KS equation can be written as

$$\sum_{q}^{\text{all}} (F_{pq\sigma}D_{qr\sigma} - D_{pq\sigma}F_{qr\sigma}) = i\frac{\partial D_{pr\sigma}}{\partial t}, \tag{1}$$

$$\sum_{q}^{\text{all}} D_{pq\sigma}D_{qr\sigma} = D_{pr\sigma}, \tag{2}$$

where D is a density matrix and F is the KS Hamiltonian matrix, both labeled by spin index σ. The exact-exchange KS Hamiltonian operator is defined as

$$F_\sigma = -\frac{1}{2}\nabla_1^2 + V_{\text{ext.}}(\mathbf{r}_1) + \sum_{\tau}^{\alpha,\beta}\int \frac{\rho_\tau(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_2 + V_\sigma^{\text{OEP}}(\mathbf{r}_1), \tag{3}$$

where $V_{\text{ext.}}(\mathbf{r})$ is a spin-independent external potential (e.g., the nuclear potential), $\rho_\tau(\mathbf{r})$ is the τ-spin electron density, and $V_\sigma^{\text{OEP}}(\mathbf{r})$ is the σ-spin OEP. The OEP contains only the exact exchange part and should be distinguished from correlated OEP considered elsewhere.

The matrix elements of the OEP are computed by the following formula:

$$V_{pq\sigma}^{\text{OEP}} = V_{pq\sigma}^{S} - 2\sum_{i}^{\text{occ}}\sum_{a}^{\text{vir}}\sum_{\kappa,\lambda}^{\text{aux}} \frac{(K_{ia\sigma}+V_{ia\sigma}^{S})(i_\sigma a_\sigma \kappa)(p_\sigma q_\sigma \lambda)}{\varepsilon_{i\sigma}-\varepsilon_{a\sigma}}(\mathbf{X}_\sigma^{-1})_{\kappa\lambda}, \tag{4}$$

with the three-center overlap integrals involving the orthonormal auxiliary basis functions $\{\chi_\kappa(\mathbf{r})\}$ being

$$(p_\sigma q_\sigma \kappa) = \int \varphi_{p\sigma}(\mathbf{r})\varphi_{q\sigma}(\mathbf{r})\chi_\kappa(\mathbf{r})d\mathbf{r}. \tag{5}$$

A set of even-tempered primitive Gaussian functions, after canonical orthogonalization, may be used as the auxiliary functions [38]. In Eq. (4), we add and subtract the Slater potential $V_\sigma^S(\mathbf{r})$ to ensure the correct $-1/r$ asymptotic decay. The Slater potential is defined analytically by

$$V_\sigma^S(\mathbf{r}_1) = -\sum_{i,j}^{\text{occ}} \frac{\varphi_{i\sigma}(\mathbf{r}_1)\varphi_{j\sigma}(\mathbf{r}_1)}{\rho_\sigma(\mathbf{r}_1)}\int \frac{\varphi_{i\sigma}(\mathbf{r}_2)\varphi_{j\sigma}(\mathbf{r}_2)}{|\mathbf{r}_1-\mathbf{r}_2|}d\mathbf{r}_2, \tag{6}$$

with its matrix representation being

$$V_{pq\sigma}^{S} = \int \varphi_{p\sigma}(\mathbf{r})V_\sigma^S(\mathbf{r})\varphi_{q\sigma}(\mathbf{r})d\mathbf{r}, \tag{7}$$

where $\varphi_{p\sigma}(\mathbf{r})$ is the pth σ-spin KS orbital. The matrix K in Eq. (4) is the HF exchange and its elements are given by

$$K_{ia\sigma} = \sum_{j}^{\text{occ}} (i_\sigma j_\sigma | j_\sigma a_\sigma), \tag{8}$$

where the two-electron integrals are, as usual,

$$(p_\sigma q_\sigma | r_\tau s_\tau) = \int \int \frac{\varphi_{p\sigma}(\mathbf{r}_1)\varphi_{q\sigma}(\mathbf{r}_1)\varphi_{r\tau}(\mathbf{r}_2)\varphi_{s\tau}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \tag{9}$$

The matrix $\mathbf{X}_\sigma$ is the auxiliary-basis-set representation of the σ-spin linear response function in the adiabatic approximation—i.e.,

$$X_\sigma(\mathbf{r}_1,\mathbf{r}_2) = 2\sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} \frac{\varphi_{i\sigma}(\mathbf{r}_1)\varphi_{a\sigma}(\mathbf{r}_1)\varphi_{i\sigma}(\mathbf{r}_2)\varphi_{a\sigma}(\mathbf{r}_2)}{\varepsilon_{i\sigma} - \varepsilon_{a\sigma}}, \tag{10}$$

$$(\mathbf{X}_\sigma)_{\kappa\lambda} = 2\sum_{i}^{\text{occ}} \sum_{a}^{\text{vir}} \frac{(i_\sigma a_\sigma \kappa)(i_\sigma a_\sigma \lambda)}{\varepsilon_{i\sigma} - \varepsilon_{a\sigma}}, \tag{11}$$

where $\varepsilon_{p\sigma}$ is the KS orbital energy of $\varphi_{p\sigma}(\mathbf{r})$.

The corresponding energy functional of the OEP method is the HF energy expression. Equation (4) can indeed be derived as the functional derivative of the energy functional with respect to electron density, with the constraint that the potential be local. For spin-unpolarized two-electron systems, $V_\sigma^{\text{OEP}} = V_\sigma^S$ and the HF and OEP total energies agree identically. For systems with more than two electrons, the OEP total energies are slightly higher than the HF ones, reflecting the additional constraint in the variational method.

III. EXACT-EXCHANGE TDDFT

When we add to the KS Hamiltonian (3) a time-dependent perturbation whose matrix elements are $h_{pq\sigma}\{\exp(-i\omega t) + \exp(i\omega t)\}$ with

$$h_{pq\sigma} = \int \varphi_{p\sigma}(\mathbf{r}) z \varphi_{q\sigma}(\mathbf{r}) d\mathbf{r} \tag{12}$$

and z being a dipole perturbation operator, the linear time-dependent response $d_{pq\sigma}^{[-\omega]} \exp(-i\omega t) + d_{pq\sigma}^{[+\omega]} \exp(i\omega t)$ (and also higher-order ones) can be observed in the density matrix elements $D_{pq\sigma}$ in Eqs. (1) and (2). The amplitudes d of the linear response can be obtained by solving the coupled-perturbed or time-dependent OEP equations of the form

$$\begin{aligned}(\varepsilon_{a\sigma} - \varepsilon_{i\sigma}) d_{ai\sigma}^{[-\omega]} + h_{ai\sigma} + \sum_{b}^{\text{vir}} \sum_{j}^{\text{occ}} \sum_{\tau}^{\alpha,\beta} \{ (a_\sigma i_\sigma ||| j_\tau b_\tau) d_{bj\tau}^{[-\omega]} \\ + (a_\sigma i_\sigma ||| b_\tau j_\tau) d_{bj\tau}^{[+\omega]} \} = \omega d_{ai\tau}^{[-\omega]},\end{aligned} \tag{13}$$

$$\begin{aligned}(\varepsilon_{i\sigma} - \varepsilon_{a\sigma}) d_{ai\sigma}^{[+\omega]} - h_{ia\sigma} - \sum_{b}^{\text{vir}} \sum_{j}^{\text{occ}} \sum_{\tau}^{\alpha,\beta} \{ (i_\sigma a_\sigma ||| j_\tau b_\tau) d_{bj\tau}^{[-\omega]} \\ + (i_\sigma a_\sigma ||| b_\tau j_\tau) d_{bj\tau}^{[+\omega]} \} = \omega d_{ai\tau}^{[+\omega]},\end{aligned} \tag{14}$$

where we used the relation $d_{ai\sigma}^{[+\omega]} = d_{ia\sigma}^{[-\omega]}$. These may be translated into a compact matrix linear equation

$$\begin{pmatrix} \mathbf{A} - \omega \mathbf{1} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} + \omega \mathbf{1} \end{pmatrix} \begin{pmatrix} \mathbf{d}^{[-\omega]} \\ \mathbf{d}^{[+\omega]} \end{pmatrix} = - \begin{pmatrix} \mathbf{h} \\ \mathbf{h} \end{pmatrix}, \tag{15}$$

with

$$A_{ai\sigma,bj\tau} = \delta_{ij}\delta_{ab}\delta_{\sigma\tau}(\varepsilon_{a\sigma} - \varepsilon_{i\tau}) + (a_\sigma i_\sigma ||| j_\tau b_\tau), \tag{16}$$

$$B_{ai\sigma,bj\tau} = (a_\sigma i_\sigma ||| b_\tau j_\tau), \tag{17}$$

and $\mathbf{1}$ is a unit matrix. Once these equations are solved for d, the dynamic polarizability is readily evaluated from

$$\alpha(-\omega; +\omega) = -2 \sum_{a}^{\text{vir}} \sum_{i}^{\text{occ}} \sum_{\sigma}^{\alpha,\beta} (h_{ai\sigma} d_{ai\sigma}^{[-\omega]} + h_{ai\sigma} d_{ai\sigma}^{[+\omega]}). \tag{18}$$

In the above, we have introduced a shorthand notation of the sum of two-electron integrals

$$(p_\sigma q_\sigma ||| r_\tau s_\tau) = (p_\sigma q_\sigma | r_\tau s_\tau) + (p_\sigma q_\sigma | f_{\sigma\tau}^{\text{OEP}} | r_\tau s_\tau), \tag{19}$$

where the second term

$$\begin{aligned}(p_\sigma q_\sigma | f_{\sigma\tau}^{\text{OEP}} | r_\tau s_\tau) = \int \int \varphi_{p\sigma}(\mathbf{r}_1)\varphi_{q\sigma}(\mathbf{r}_1) f_{\sigma\tau}^{\text{OEP}}(\mathbf{r}_1,\mathbf{r}_2) \\ \times \varphi_{r\tau}(\mathbf{r}_2)\varphi_{s\tau}(\mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2\end{aligned} \tag{20}$$

involves the exchange kernel or the functional derivative of the OEP with respect to spin density,

$$f_{\sigma\tau}^{\text{OEP}}(\mathbf{r}_1,\mathbf{r}_2) = \delta_{\sigma\tau} \frac{\delta V_\sigma^{\text{OEP}}(\mathbf{r}_1)}{\delta \rho_\tau(\mathbf{r}_2)}, \tag{21}$$

within the adiabatic approximation. These two-electron integrals are computed, with the aid of the orthonormal auxiliary basis set, by evaluating the formula [41]

$$\begin{aligned}(p_\sigma q_\sigma | f_{\sigma\tau}^{\text{OEP}} | r_\tau s_\tau) = \delta_{\sigma\tau} \sum_{\kappa,\lambda,\mu,\nu}^{\text{aux}} (p_\sigma q_\sigma \kappa) \\ \times (\mathbf{X}_\sigma^{-1})_{\kappa\lambda} (\mathbf{g}_\sigma)_{\lambda\mu} (\mathbf{X}_\sigma^{-1})_{\mu\nu} (r_\sigma s_\sigma \nu),\end{aligned} \tag{22}$$

with

$$\begin{aligned}(\mathbf{g}_\sigma)_{\lambda\mu} = & -2\sum_{i}^{\text{occ}} \sum_{a,b}^{\text{vir}} \frac{(K_{ba\sigma} + V_{ba\sigma}^{\text{OEP}})}{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{i\sigma} - \varepsilon_{b\sigma})} (i_\sigma a_\sigma \lambda)(i_\sigma b_\sigma \mu) \\ & + 2\sum_{i,j}^{\text{occ}} \sum_{a}^{\text{vir}} \frac{(K_{ij\sigma} + V_{ij\sigma}^{\text{OEP}})}{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{j\sigma} - \varepsilon_{a\sigma})} (i_\sigma a_\sigma \lambda)(a_\sigma j_\sigma \mu) \\ & - 2\sum_{i}^{\text{occ}} \sum_{a,b}^{\text{vir}} \frac{(K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}})}{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{i\sigma} - \varepsilon_{b\sigma})} (b_\sigma a_\sigma \lambda)(i_\sigma b_\sigma \mu) \\ & - 2\sum_{i}^{\text{occ}} \sum_{a,b}^{\text{vir}} \frac{(K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}})}{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{i\sigma} - \varepsilon_{b\sigma})} (i_\sigma b_\sigma \lambda)(b_\sigma a_\sigma \mu) \\ & + 2\sum_{i,j}^{\text{occ}} \sum_{a}^{\text{vir}} \frac{(K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}})}{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{j\sigma} - \varepsilon_{a\sigma})} (i_\sigma j_\sigma \lambda)(a_\sigma j_\sigma \mu) \\ & + 2\sum_{i,j}^{\text{occ}} \sum_{a}^{\text{vir}} \frac{(K_{ia\sigma} + V_{ia\sigma}^{\text{OEP}})}{(\varepsilon_{i\sigma} - \varepsilon_{a\sigma})(\varepsilon_{j\sigma} - \varepsilon_{a\sigma})} (a_\sigma j_\sigma \lambda)(i_\sigma j_\sigma \mu)\end{aligned}$$

TABLE I. The average static polarizability $\alpha(0)$ and anisotropy of the static polarizability $\gamma(0)=2^{-1/2}\{(\alpha_{xx}-\alpha_{yy})^2+(\alpha_{yy}-\alpha_{zz})^2+(\alpha_{zz}-\alpha_{xx})^2\}^{1/2}$ (in a.u.).

System	Quantity	SVWN	BLYP	B3LYP	SVWN/AC	HF	OEP	Expt.[g]
He[a]	$\alpha(0)$	1.66	1.57	1.51	1.39	1.32	1.32	1.38
Ne[b]	$\alpha(0)$	3.05	3.10	2.88	2.54	2.38	2.37	2.67
Ar[c]	$\alpha(0)$	12.0	12.1	11.7	12.0	10.7	10.7	11.07
H_2[d]	$\alpha(0)$	5.96	5.73	5.59	5.44	5.27	5.27	5.428
FH[e]	$\alpha(0)$	5.80	5.88	5.52	4.96	4.72	4.70	5.601
N_2[f]	$\alpha(0)$	11.7	11.8	11.5	11.1	11.0	11.0	11.74
H_2[d]	$\gamma(0)$	1.93	1.95	1.92	1.71	1.87	1.87	2.04
FH[e]	$\gamma(0)$	1.53	1.59	1.57	1.32	1.52	1.50	1.33
N_2[f]	$\gamma(0)$	5.52	5.70	5.69	5.35	6.04	6.02	4.45

[a] The 12*s*8*p*5*d* even-tempered basis set with exponents $10^{n/2}$ ($n=6,\ldots,-5$ for *s* type; $n=2,\ldots,-5$ for *p* type; $n=1,\ldots,-3$ for *d* type).

[b] The 15*s*10*p*7*d* even-tempered basis set with exponents $10^{n/2}$ ($n=9,\ldots,-5$ for *s* type; $n=4,\ldots,-5$ for *p* type; $n=3,\ldots,-3$ for *d* type).

[c] The 17*s*12*p*8*d* even-tempered basis set with exponents $10^{n/2}$ ($n=11,\ldots,-5$ for *s* type; $n=6,\ldots,-5$ for *p* type; $n=4,\ldots,-3$ for *d* type).

[d] The 9*s*6*p*2*d* even-tempered basis set with exponents $10^{n/2}$ ($n=4,\ldots,-4$ for *s* type; $n=1,\ldots,-4$ for *p* type; $n=0,-1$ for *d* type). The H-H distance was 0.7461 Å.

[e] See footnote d for the hydrogen basis set and footnote f for the fluorine basis set. The F-H distance was 0.9170 Å.

[f] The 14*s*9*p*3*d* even-tempered basis set with exponents $10^{n/2}$ ($n=8,\ldots,-5$ for *s* type; $n=3,\ldots,-5$ for *p* type; $n=1,0,-1$ for *d* type). The N-N distance was 1.0976 Å.

[g] Adopted from Refs. [60,63].

$$-2\sum_{i,j}^{\text{occ}}\sum_{a,b}^{\text{vir}}\frac{(i_\sigma b_\sigma|j_\sigma a_\sigma)}{(\varepsilon_{i\sigma}-\varepsilon_{a\sigma})(\varepsilon_{j\sigma}-\varepsilon_{b\sigma})}(i_\sigma a_\sigma\lambda)(j_\sigma b_\sigma\mu)$$
$$-2\sum_{i,j}^{\text{occ}}\sum_{a,b}^{\text{vir}}\frac{(i_\sigma j_\sigma|b_\sigma a_\sigma)}{(\varepsilon_{i\sigma}-\varepsilon_{a\sigma})(\varepsilon_{j\sigma}-\varepsilon_{b\sigma})}(i_\sigma a_\sigma\lambda)(j_\sigma b_\sigma\mu). \tag{23}$$

The derivation of the exact exchange kernel in the adiabatic approximation can be found in Ref. [41]. The fourfold summation in Eq. (22) can be carried out stepwise.

IV. RESULTS AND DISCUSSION

The Gaussian-basis-set OEP and TDOEP methods have been implemented into the POLYMER program, employing the combined Colle-Nesbet [57] and *S* algorithms outlined above and the trial-vector algorithm of Pople *et al.* [58] to avoid the computation and storage of two-electron integrals in the KS orbital basis. The other algorithmic details can be found in Refs. [38,41].

In the first six rows of Table I, we compiled the static polarizabilities of He, Ne, Ar, H_2, FH, and N_2 (as representative examples of atoms and molecules having either low-lying Rydberg or valence excited states) computed by TDDFT with local [Slater-Vosko-Wilk-Nusair (SVWN)], gradient-corrected [Becke-Lee-Yang-Parr (BLYP)], hybrid [Becke3-Lee-Yang-Parr (B3LYP)], and asymptotically corrected functionals, by TDHF, and by the TDOEP in conjunction with even-tempered Gaussian functions. Generally, TDDFT with SVWN, BLYP, and B3LYP functionals overestimates the polarizabilities. The cause of this is now well known to be the wrong asymptotic decay of the exchange-correlation potentials, which is in turn related to the spurious self-interaction in DFT. Accordingly, the degree of overestimation is greater for atomic systems and H_2 than for FH and N_2, because the low-lying excited states of the former group are invariably of the diffuse, Rydberg type, which are more sensitive to the potentials in the asymptotic region. Also, the overestimation is much less for B3LYP, which has 20% of HF exchange that partially alleviates this problem. When the $-1/r$ tail of the Slater potential is spliced to the SVWN exchange-correlation potential in the asymptotic region (after the SVWN potential is shifted down by an adequate amount to ensure the seamless splicing), the resulting SVWN-AC (AC standing for the asymptotic correction) reproduces the experimental data much more accurately, with the exception of FH.

The TDHF and TDOEP methods are free from self-interaction error. As such, they provide calculated polarizabilities that look more consistent than the TDDFT (excluding TDOEP) ones in comparison to the experimental data. The OEP method, having an identical energy functional as the HF method, exhibits essentially the same time-dependent response as HF to the perturbation. The TDOEP polarizabilities are identical to the TDHF ones for He and H_2, and they are very close (within 1% of each other) for the other systems. The TDHF and TDOEP methods (but *not* TDDFT with conventional local, gradient-corrected, or hybrid functionals) are the most suitable bases for systematic correlation treatment for properties within the *ab initio* WFT and DFT frameworks, respectively.

The last three rows of Table I are the anisotropy of the average static polarizabilities. The calculated values of this quantity do not exhibit a simple pattern, unlike the average static polarizabilities themselves, which are uniformly overestimated by TDDFT (excluding the TDOEP). It appears that the cancellation of errors makes the calculated TDDFT anisotropy better agree with the experimental data. The agree-

TABLE II. The average static polarizability and anisotropy of the static polarizability in the sum-over-states (SOS) approximation (in a.u.).

System	Quantity	SVWN	BLYP	B3LYP	SVWN/AC	HF	OEP	Expt.[g]
He[a]	$\alpha_{\mathrm{SOS}}(0)$	1.81	1.74	1.52	1.53	1.00	1.49	1.38
Ne[b]	$\alpha_{\mathrm{SOS}}(0)$	3.48	3.61	3.08	2.93	1.97	2.84	2.67
Ar[c]	$\alpha_{\mathrm{SOS}}(0)$	18.0	18.4	15.7	18.0	10.1	17.0	11.07
H_2[d]	$\alpha_{\mathrm{SOS}}(0)$	7.31	7.13	6.06	6.73	3.86	6.59	5.428
FH[e]	$\alpha_{\mathrm{SOS}}(0)$	7.36	7.58	6.36	6.34	3.96	6.16	5.601
N_2[f]	$\alpha_{\mathrm{SOS}}(0)$	21.1	21.3	17.8	20.5	11.1	19.9	11.74
H_2[d]	$\gamma_{\mathrm{SOS}}(0)$	3.94	3.99	3.15	3.56	1.60	3.35	2.04
FH[e]	$\gamma_{\mathrm{SOS}}(0)$	3.28	3.45	2.79	2.79	1.49	2.83	1.33
N_2[e]	$\gamma_{\mathrm{SOS}}(0)$	19.2	19.8	15.3	19.1	7.49	17.1	4.45

[a] See the corresponding footnotes of Table I.
[b] See the corresponding footnotes of Table I.
[c] See the corresponding footnotes of Table I.
[d] See the corresponding footnotes of Table I.
[e] See the corresponding footnotes of Table I.
[f] See the corresponding footnotes of Table I.
[g] Adopted from Refs. [60,63].

ment between the TDHF and TDOEP remains very accurate.

Table II lists the average static polarizabilities and their anisotropy within the sum-over-states (SOS) approximation, which is also equivalent to the uncoupled DFT, HF, OEP, etc. The approximation amounts to neglecting two-electron integrals in the complete TDDFT, TDHF, or TDOEP equations, which simplifies the polarizabilities to an analytic form of

$$\alpha_{\mathrm{SOS}}(-\omega;+\omega) = 2\sum_{a}^{\mathrm{vir}}\sum_{i}^{\mathrm{occ}}\sum_{\sigma}^{\alpha,\beta}\left(\frac{h_{ai\sigma}^{2}}{\varepsilon_{a\sigma}-\varepsilon_{i\sigma}-\omega} + \frac{h_{ai\sigma}^{2}}{\varepsilon_{a\sigma}-\varepsilon_{i\sigma}+\omega}\right). \tag{24}$$

Generally, this is a severe approximation, resulting in significant errors from the corresponding complete TDDFT, TDHF, or TDOEP solutions. The physical meaning of virtual orbitals is different between KS DFT (including the OEP) and HF. All orbitals of KS DFT are generated by the $(N-1)$-electron potential with the energy differences between virtual and occupied orbitals being better related to excitation energies [59]. In contrast, the HF occupied and virtual orbitals correspond to qualitatively different potentials: the occupied orbitals to the $(N-1)$-electron potential and the virtual orbitals to the N-electron potential. Hence the energy differences between HF virtual and occupied orbitals are ionization potential minus electron affinity, a quantity distinctly different from (generally greater than) excitation energies. The diagonal elements of the **A** matrix in the TDHF equation are better approximated by $\varepsilon_{a\sigma}-\varepsilon_{i\sigma}-(a_\sigma a_\sigma|i_\sigma i_\sigma)$ rather than by $\varepsilon_{a\sigma}-\varepsilon_{i\sigma}$.

Because of this difference, the TDOEP (as the exact-exchange TDDFT) deviates significantly from the TDHF theory, once the SOS approximation is invoked. Invariably, the TDOEP results become much greater than the TDHF ones and are often close to the SVWN-AC values. Owing to the underestimation of the virtual orbital energies, the SVWN and BLYP values are even greater than the TDOEP or SVWN-AC ones. It may be rationalized that, because the KS orbital energy differences $\varepsilon_{a\sigma}-\varepsilon_{i\sigma}$ are physically interpreted as excitation energies, the SOS approximation is physically sounder for TDDFT (including the TDOEP). In other words, the SOS approximation in the TDHF theory involves an extra approximation of using $\varepsilon_{a\sigma}-\varepsilon_{i\sigma}$ instead of $\varepsilon_{a\sigma}-\varepsilon_{i\sigma}-(a_\sigma a_\sigma|i_\sigma i_\sigma)$. This argument seems to be supported only by the results for smaller molecules, whose TDOEP results with and without the SOS approximation agree with each other more accurately.

For the dispersion of dynamic polarizabilities also, the predicted values from the TDOEP accurately parallel those from the TDHF theory (Table III). The two methods agree identically, as they should, for spin-unpolarized two-electron systems. The TDOEP and TDHF results are in more uniformly good agreement with the experimental data, again with the exception of FH. The wrong asymptotic behavior in SVWN and BLYP (and to a lesser degree in B3LYP also) results in the overestimation of the dispersion as well as the absolute values of the dynamic polarizabilities. Consequently, the SVWN and BLYP predictions of $S(-4)$ are significantly greater than the TDHF or TDOEP values or experimental data for all but FH. It is remarkable that the asymptotic correction is equally effective for the dispersion of dynamic polarizabilities. The anomaly for FH at the TDHF level has been known and is not due to the insufficient basis set size [60]. The closer agreement between SVWN and experimental result of $S(-4)$ of FH is a coincidence as attested to by the corresponding SVWN-AC value that is closer to the TDHF one.

V. CONCLUSIONS

We have presented analytical calculations of static and dynamic polarizabilities applicable to general atomic and

TABLE III. The Cauchy moment of the dynamic polarizability $S(-4)=\partial\alpha(\omega)/\partial(\omega^2)$ (in a.u.).

System	SVWN	BLYP	B3LYP	SVWN/AC	HF	OEP	Expt.[f]
He[a]	2.4	2.2	2.0	1.6	1.4	1.4	1.6
Ne[b]	4.4	4.8	3.8	2.4	2.1	2.1	3.0
Ar[c]	36	39	33	36	25	26	29
H_2[d]	25	24	22	20	19	19	19.96
FH[e]	16	17	13	8.9	7.8	7.9	14.40

[a] See the corresponding footnotes of Table I.
[b] See the corresponding footnotes of Table I.
[c] See the corresponding footnotes of Table I.
[d] See the corresponding footnotes of Table I.
[e] See the corresponding footnotes of Table I.
[f] Adopted from Refs. [60,63].

molecular systems with an exact exchange functional of KS DFT through the adiabatic TDOEP formalism. It has been shown that the rigorous exchange treatment in the TDOEP and TDHF theory yield polarizabilities that agree closely with each other (typically within 1%). This is in contrast to previous approximate or semiempirical exchange functionals in TDDFT (such as Slater, Becke88, etc.) that generally overestimate polarizabilities and their dispersion, sometimes by 100% relative to the TDHF theory.

Apart from offering a stable method for computing polarizabilities at the exact exchange *ab initio* DFT, this LCAO Gaussian-basis-set algorithm of the TDOEP will serve as the key methodological development for the future extension to the inexpensive inclusion of electron correlation to properties through correlated orbitals and orbital energies obtained from second-order MBPT correlated *ab initio* DFT [19–22]. It is also essential for locating all excited-state roots of the TDOEP with a frequency-dependent kernel as the poles of the frequency-dependent polarizabilities [61,62]. An outstanding question is whether dominant two-electron excitations come into the solution manifolds of the TDOEP by introducing frequency dependence in the kernel.

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