A new framework for frequency-dependent polarizable force fields

YingXing Cheng and Toon Verstraelen

Center for Molecular Modeling (CMM), Ghent University - Technologiepark-Zwijnaarde 46, B-9052 Gent, Belgium

(*Electronic mail: toon.verstraelen@ugent.be)

(Dated: 7 September 2022)

A frequency-dependent extension of the polarizable force field “Atom-Condensed Kohn-Sham density functional theory approximated to the second-order” (ACKS2) [J. Chem. Phys. 141, 194114 (2014)] is proposed, referred to as ACKS2$\omega$. The method enables theoretical predictions of dynamical response properties of finite systems after a partitioning of the frequency-dependent molecular response function. Parameters in this model are computed simply as expectation values of an electronic wavefunction, and the hardness matrix is entirely reused from ACKS2 as an adiabatic approximation is used. A numerical validation shows that accurate models can already be obtained with atomic monopoles and dipoles. Absorption spectra of 42 organic and inorganic molecular monomers are evaluated using ACKS2$\omega$, and our results agree well with the time-dependent DFT calculations. Also for the calculation of $C_6$ dispersion coefficients, ACKS2$\omega$ closely reproduces its TDDFT reference. When parameters for ACKS2$\omega$ are derived from a PBE/aug-cc-pVDZ ground state, it reproduces experimental values for 903 organic and inorganic intermolecular pairs with an MAPE of 3.84%. Our results confirm that ACKS2$\omega$ offers a solid connection between the quantum-mechanical description of frequency-dependent response and computationally efficient force-field models.
I. INTRODUCTION

Molecular simulation is a powerful tool to investigate and predict the properties and dynamics of a wide range of finite and condensed-phase systems. Different levels of theory for such simulations can be roughly divided into two categories: quantum-mechanical (QM) electric structure methods and force-field (FF) methods. Kohn-Sham Density Functional Theory (DFT) offers a good trade-off between computational efficiency and accuracy, which has been successfully applied to study both ground and excited state properties of inorganic and organic molecular systems. However, Kohn-Sham DFT (with density fitting) has an $O(N^3)$ computational complexity where $N$ is the number of basis functions, which impedes its application to large-scale systems, especially for molecular dynamics (MD) simulations. On the other hand, FF methods, only using a set of functions of molecular geometry with several empirical parameters to determine molecular energy, have been developed and applied to large-scale MD simulations. In general, FF methods have a much lower computational cost than QM methods, at the expense of a reduced, yet acceptable, computational accuracy. One significant problem in traditional FF methods is the lack of electronic polarization, i.e., the response of the electron distribution to the environment, which led the molecular modeling community to develop polarizable force fields (PFFs)\textsuperscript{1–12} to improve the predictive accuracy of long-range interactions by adding explicit polarization effects.

Classical PFF models can be classified into four broad categories: induced dipoles or multipoles,\textsuperscript{1–5} the Drude oscillator\textsuperscript{6–8} (also known as “core-shell”\textsuperscript{13} or “charge-on-spring”\textsuperscript{14}), Electronegativity Equalization Method (EEM),\textsuperscript{9,10} and the explicit electron model.\textsuperscript{11,12} It should be noted that several models similar to the EEM exist, such as fluctuating charges (FQ or FlucQ),\textsuperscript{15–19} charge equilibration (QE, QE\textsuperscript{20} or CHEQ\textsuperscript{21}), and chemical potential equalization (CPE)\textsuperscript{22}. Note that EEM is often not considered to be a proper PFF: because it only uses variable atomic charges, it cannot describe out-of-plane polarization of planar molecules.\textsuperscript{22} One can represent these effects in EEM by including additional off-nuclear sites.\textsuperscript{23–25} This leads to slightly more expensive models and additional model choices, such as the location of the extra sites and the associated parameters. Here, we will treat EEM on the same footing as other PFFs because its mathematical structure is completely analogous.

The EEM was first developed by Mortier \textit{et al.} from basic DFT equations according to Sanderson’s principle of electronegativity equalization,\textsuperscript{26} i.e., electrons flow until all electronegativities are equalized during the formation of a molecule. The ability of EEM (or one of its close rela-
tives) to predict ground-state charge distributions has been validated extensively, e.g. for inorganic liquids,\(^{16}\) inorganic solids,\(^{27-29}\) organic molecules,\(^{18,30-32}\) and biomolecular systems.\(^{19,33-35}\) One appealing aspect of the EEM is that atomic monopolar fluctuations are included, and that one may systematically extend it with higher atomic multipoles, as in CPE.\(^{22}\) However, the EEM also has two fundamental issues in simulations of extended systems or charge transfer during chemical reactions as follows:\(^{36-40}\) (1) the EEM always predicts a cubic scaling of the dipole polarizability with system size, which is not correct for dielectric systems where a linear scaling exists in the macroscopic limit; (2) EEM obtains fractional molecular charges even when two molecules are well separated and gives a slowly decaying intermolecular charge transfer. The main reason for both problems is that long-range charge flow is always allowed in EEM, which is only realistic in metallic systems. Shortly after these shortcomings were first discussed in the literature, several \textit{ad hoc} improvements were proposed, for instance, by applying artificial constraints to molecular charges\(^{18,38}\) or dipoles,\(^{41}\) or introducing a distance-dependent function to penalize long-range charge transfer.\(^{42}\) Later, more consistent models were proposed, such as the split-charge equilibration (SQE): by adding a bond-hardness term to EEM, SQE becomes capable of modeling dielectric materials.\(^{37,39}\)

Recently, Verstraelen \textit{et al.} developed a new polarizable force field (PFF), namely Atom-Condensed Kohn-Sham DFT approximated to second-order (ACKS2),\(^{40}\) which has been validated and applied to molecular systems, and which addresses both fundamental issues of the EEM. ACKS2 improves upon the EEM by adding an electronic kinetic energy term via the Legendre transform of the Kohn-Sham kinetic energy, enabling one to expand the kinetic energy to second-order in the atomic populations and atomic Kohn-Sham potentials. It was shown that this new kinetic energy term is equivalent to the bond-hardness energy in the SQE. Later, a generalization of the ACKS2 model for arbitrary variational wavefunctions was proposed.\(^{43}\) The ACKS2 formalism was numerically validated by a direct computation of the ACKS2 parameters from a reference Kohn-Sham DFT calculation. With these parameters, the static linear response properties of molecules obtained with an underlying theory, e.g., Kohn-Sham DFT, can be reproduced precisely in the limit of a complete basis sets for density and potential fluctuations.

To use ACKS2 for approximate polarization energy calculations, a tailored empirical parameterization was incorporated into ReaxFF, as an alternative to the EEM, which turned out to be essential in the development of eReaxFF.\(^{44}\) Later, Gütlein \textit{et al.} developed a new PFF using Gaussian basis sets, based on the ACKS2 model,\(^{45}\) where generic parameters were proposed for
elements C and H, such as widths of Gaussian basis functions. This parametrization can predict
DFT data, such as response properties and interaction energies, of a series of hydrocarbons. Later,
they proposed two ACKS2 variants, f-ACKS2 and scf-ACKS2, to handle condensed phases by
dividing them into molecular fragments, which are coupled by Coulomb interactions.\textsuperscript{46}

This work extends ACKS2 to the time- and frequency-dependent domain to compute the
dynamical response properties of finite molecules, e.g., frequency-dependent polarizabilities, $C_6$
dispersion coefficients, and molecular absorption spectra. The resulting ACKS2\textsubscript{ω} model, through
its use of atomic multipole expansions, allows one to investigate the contribution of charge-flow
effects on dynamic response properties, which is a topic of ongoing research. One of the fu-
ture applications envisioned for ACKS2\textsubscript{ω} is an efficient approximation of the non-local disper-
sion energy, i.e. for which interatomic charge fluctuations become important,\textsuperscript{47–54} such as carbon
nanomaterials,\textsuperscript{48,49} traditional semiconductors,\textsuperscript{50,51} and low-dimensional materials.\textsuperscript{48,52–54} To our
best knowledge, the time-dependent or frequency-dependent extension of ACKS2 has not been
investigated yet.

The derivation of ACKS2\textsubscript{ω} relies on time-dependent DFT (TDDFT). TDDFT has received
much attention in recent decades because of its good trade-off between numerical efficiency and
accuracy compared to wavefunction-based methods. The standard formalism of TDDFT builds
on the Runge-Gross theorem,\textsuperscript{55} stating that there exists a one-to-one correspondence between
densities and potentials for any fixed initial many-body state. TDDFT uses many DFT concepts,
e.g. the whole interacting many-body system is replaced by a non-interacting Kohn-Sham system
that shares the same density. However, it also has unique requirements, such as the initial state
dependence and time-dependent exchange-correlation functional. Readers are referred to recent
books\textsuperscript{56,57} and review articles\textsuperscript{58–61} for further details about TDDFT. Within the TDDFT regime,
the linear response of the electron density can be calculated precisely, assuming one disposes of
the exact exchange-correlation functional. In practice, TDDFT is a useful and relatively simple
scheme to compute molecular linear-response properties.\textsuperscript{62–66}

To derive the ACKS2\textsubscript{ω} model, we use a quasi-energy formalism, also known as the Floquet
theory, which is often used in time-dependent response model development\textsuperscript{66–72} and can be seen
as a special case of TDDFT.\textsuperscript{55,73} The benefits of the quasi-energy language have been discussed
elsewhere.\textsuperscript{72} One of the advantages of quasi-energy DFT is that the initial state dependence of
the Runge-Gross theorem is not necessary anymore, and instead a periodic boundary condition is
applied to an external perturbation. Moreover, the quasi-energy ansatz enables a unified frame-
work for dynamic linear-response property calculations based on wavefunction and DFT methods, as it is generally valid for both variational and non-variational methods. This allows dynamical response properties to be derived by the virtues of the energy derivative approach using the quasi-energy formalism. However, the validity of Floquet theory has been a point of discussion elsewhere and principle requires the following approximations: (i) a finite basis is employed; (ii) the driving external perturbation is weak and off-resonant. Point (i) ensures an adiabatic limit exists for the “Floquet ground state”, on which the energy minimum principle is valid, and the latter determines the one-to-one density-potential mapping. Point (ii) suggests that Floquet theory is only a proper approximate method to treat linear-response problems. Nonetheless, for molecular force-field development, these two conditions are generally satisfied; thus, one can still use Floquet theory to develop frequency-dependent force-field methods.

The goal of this paper is to introduce ACKS2 as a model with a structure reminiscent of conventional PFFs, yet with all parameters defined in terms of an underlying electronic structure theory. This direct connection to electronic structure theory assures a solid foundation for more pragmatic parameterizations of frequency-dependent PFFs. The main distinction with the work of Misquitta and Stone, e.g. ISA-Pol, is that ACKS2 explicitly describes the transformation from non-interacting to interacting response functions through electron-electron interactions, whereas ISA-Pol directly models the interacting response relying on time-dependent Hartree-Fock or TDDFT results. Potential applications of frequency-dependent PFFs include modeling of optical spectra of complex systems at a force-field cost, approximations of dispersion in force fields, computationally efficient non-local dispersion corrections including many-body effects for DFT calculations or frequency-dependent polarizable embedding. In this paper, ACKS2 parameters are always computed from a Kohn-Sham DFT calculation for any given molecular geometry. This leads to relatively accurate and expensive parameterizations of test systems, primarily intended to validate the ACKS2 equations. Obviously, for large-scale simulations, more efficient parameterizations should be developed, not involving a prior Kohn-Sham DFT calculation, for which machine-learning approaches have shown promising results.

A benchmark database including 42 inorganic and organic molecules from Ref. 87, referred to as TS42, is used for a numerical validation of the ACKS2 model. First, the absorption spectra of the 42 molecules are investigated using ACKS2 in comparison to TDDFT calculations. Then, the $C_6$ dispersion coefficients are compared against experimental data and Tkatchenko-Scheffler van der Waals method (called TS in what follows). More specifically, the accuracy of the
ACKS2ω model is tested by checking the $C_6$ coefficients of 903 molecular pairs constructed from the database. Furthermore, we also compare the performance of ACKS2ω to the range-separated calculations of Toulouse et al. on 27 homodimers from a subset of TS42, referred to hereafter as the TS27 database.

The remainder of this paper is organized as follows: the basic theory of the ACKS2ω model is introduced in Section II, followed by computational details of the numerical validation in Section III. Results and discussion are presented in Section IV. A summary is given in Section V. Atomic units are used, unless noted otherwise.

II. THEORY

This section derives the ACKS2ω formalism from TDDFT, using the quasi-energy formalism. Hence, a brief review of the quasi-energy method is first presented in Section II A. The quasi-energy expressions have been employed in response theory because of their straightforward definition. The theory of ACKS2ω within quasi-energy ansatz is presented in Section II B, where a set of equations is derived in analogy with ACKS2. A dynamic linear-response theory is then provided in the frequency domain in Section II C. As a result, a set of linear-response equations are generated when two finite basis sets are applied (Section II D). Finally, in Section II E, we apply ACKS2ω in Kohn-Sham DFT with a semi-local exchange-correlation (xc) functional.

A. Quasi-energy formalism

The quasi-energy formalism or Floquet theory is employed in the original TDDFT derivation. The definitions of time-dependent exchange-correlation potentials and kernels are much more accessible using the quasi-energy notation. In this section, we use the notation of Salek et al. and Christiansen et al. From the time-dependent Schrödinger equation, we have

\[
\left( \hat{H} - i \frac{\partial}{\partial t} \right) |\bar{0}(t)\rangle = 0
\]

\[
\hat{H} = \hat{H}_0 + \hat{V}_1(t)
\]

where $\hat{H}_0$ and $\hat{V}_1(t)$ are the time-independent zeroth-order Hamiltonian and time-dependent perturbation operator, respectively. The exact solution of $\hat{H}_0$ is given by a ground-state calculation and perturbation theory can be developed through a generalization of the Rayleigh-Schrödinger
We consider the time-dependent perturbation theory\textsuperscript{70,78}

\[ |\tilde{0}(t)\rangle = e^{-iF(t)}|\tilde{0}(t)\rangle \] \hspace{1cm} (3)

where \( F(t) \) is a purely time-dependent function. The vector \( |\tilde{0}\rangle \) represents the complete wavefunction whose phase-isolated part is denoted by \( |\tilde{0}\rangle \), where time dependence of the vectors is understood. The time-dependent Schrödinger equation is then rewritten as

\[ \left( \hat{H} - i \frac{\partial}{\partial t} \right) |\tilde{0}\rangle = L(t)|\tilde{0}\rangle \] \hspace{1cm} (4)

in which \( L(t) = \dot{F}(t) \) is the time-dependent quasi-energy. Langhoff et al. showed that \( |\tilde{0}\rangle \) can be normalized at all times.\textsuperscript{78} Consequently, the time-dependent quasi-energy can be expressed as

\[ L(t) = \langle \tilde{0} | \hat{H} - i \frac{\partial}{\partial t} | \tilde{0} \rangle \] \hspace{1cm} (5)

In order to use Hellmann-Feynman theorem, in analogy to the static case, the external time-dependent perturbation is assumed to be periodic, i.e., \( \hat{V}_1(t) = \hat{V}_1(t + \mathcal{T}) \).\textsuperscript{72} Here, we use the symbol \( \mathcal{T} \), referred to as the time period, instead of \( T \) used in Ref. 72 to avoid ambiguity with kinetic energy functional \( T \), which is well-known in DFT or TDDFT. Using curly brackets for time-averaging,

\[ \{ f(t) \} \mathcal{T} = \frac{1}{\mathcal{T}} \int_{-\mathcal{T}/2}^{+\mathcal{T}/2} f(t) dt, \] \hspace{1cm} (6)

the quasi-energy is defined as

\[ Q = \{ L(t) \} \mathcal{T} \] \hspace{1cm} (7)

Techniques for time-independent problems, such as the variational principle\textsuperscript{70} as well as the Hellman-Feynman theorem,\textsuperscript{72} can be applied to the quasi-energy, to obtain a solution or a response to a perturbation for the time-dependent case. The quasi-energy formalism is also generally applicable to wavefunction methods and DFT\textsuperscript{71,72}, at least for weak and off-resonant perturbation and when using finite basis sets approximations.\textsuperscript{76,77}

In the context of TDDFT, the quasi-energy can be written a functional of the time-dependent density, \( \rho(r, t) \):\textsuperscript{64,72}

\[ Q[\rho] = \{ \langle \tilde{0} | \hat{H} - i \frac{\partial}{\partial t} | \tilde{0} \rangle \} \mathcal{T} = T[\rho] + V[\rho] + J[\rho] + Q_{\text{ncr}}[\rho] - S[\rho] \] \hspace{1cm} (8)

where \( T[\rho] \) and \( V[\rho] \) are the kinetic energy and the interaction with the external potential, respectively. The non-classical quasi-energy \( Q_{\text{ncr}}[\rho] \) includes the effects of exchange and correlation,
whereas $J[\rho]$ and $S[\rho]$ are formally defined by
\[
J[\rho] = \frac{1}{2} \left\{ \iint \frac{\rho(r,t)\rho(r',t)}{|r-r'|} dr dr' \right\} \mathcal{T} \tag{9}
\]
\[
S[\rho] = \left\{ \langle 0\mid i\frac{\partial}{\partial t}\mid 0 \rangle \right\} \mathcal{T} \tag{10}
\]

A more extensive discussion of the quasi-energy formalism in DFT can be found in Ref. 72, 76, and 77.

**B. Decomposition of the quasi-energy into explicit and implicit terms**

The functional in DFT can be written as the sum of a universal functional and the interaction of the electrons with external potential. The universal functional is a general term for all systems, which can be divided into two parts suggested by the ACKS2 model: the explicit functional ($E^{\text{exp}}$), which is a known functional of the density, and the implicit functional ($E^{\text{imp}}$). Similarly, in quasi-energy TDDFT the corresponding explicit functional $Q^{\text{exp}}$ and implicit functional $Q^{\text{imp}}$ are given as
\[
Q_v[\rho] = Q^{\text{exp}}[\rho] + Q^{\text{imp}}[\rho] + \left\{ \int \rho(r,t)v(r,t)dr \right\} \mathcal{T} \tag{11}
\]
The implicit functional uses an auxiliary $N$-fermion wavefunction through a constrained-search formulation
\[
Q^{\text{imp}}[\rho] = \min_{\Psi \rightarrow \rho} W[\Psi] \tag{12}
\]
With the method of Lagrange multipliers, it can also be written out explicitly
\[
Q^{\text{imp}}[\rho] = \sup_u \left( Q^0[u,N] - \left\{ \int \rho(r,t)u(r,t)dr \right\} \mathcal{T} \right) \tag{13}
\]
\[
Q^0[u,N] = \min_{\Psi} \left( W[\Psi] + \left\{ \int \rho[\Psi](r,t)u(r,t)dr \right\} \mathcal{T} \right) \tag{14}
\]
where $u(r,t)$ is a function that specifies a Lagrange multiplier at every point in terms of both space and time, and $\rho[\Psi](r,t)$ is the electron density of the auxiliary wavefunction. All terms that are dependent on the auxiliary wavefunction are collected in $Q^0[u,N]$. This quasi-energy can be interpreted as the ground-state energy of $W[\Psi]$ in a specified auxiliary potential, $u(r,t)$.

For a given external potential, $v(r,t)$, the $N$-electron ground state is solved by minimizing the following Lagrangian with respect to $\rho(r,t)$ and maximizing it with respect to $u(r,t)$ and $\mu(t)$:
\[
L_v[\rho,u,\mu] = Q_v[\rho,u] - \left\{ \mu(t) \left( \int \rho(r,t)dr - N \right) \right\} \mathcal{T} \tag{15}
\]

8
where the quasi-energy is now a functional of the density and auxiliary potential
\[
Q_v[\rho, u] = Q_{\text{exp}}[\rho] + Q^o[u, N] + \left\{ \int_\Omega \rho(r,t)[v(r,t) - u(r,t)] dr \right\}_{\rho, u}
\] (16)

Finally, the stationary point is defined by the following sets of Euler-Lagrange equations,\(^6\)
\[
\frac{\delta Q_{\text{exp}}[\rho]}{\delta \rho(r,t)} + v(r,t) - u(r,t) = \mu(t) \quad (17)
\]
\[
\frac{\delta Q^o[u, N]}{\delta u(r,t)} - \rho(r,t) = 0 \quad (18)
\]
\[
\int_\Omega \rho(r,t) dr = N \quad (19)
\]

C. Linear response

In linear-response theory, it is more convenient to first apply a Fourier-transform to all time-dependent functions,\(^5\) which yields formally similar Euler-Lagrange equations:
\[
\frac{\delta Q_{\text{exp}}[\rho]}{\delta \rho(r,\omega)} + v(r, \omega) - u(r, \omega) = \mu(\omega) \quad (20)
\]
\[
\frac{\delta Q^o[u, N]}{\delta u(r,\omega)} - \rho(r, \omega) = 0 \quad (21)
\]
\[
\int_\Omega \rho(r,\omega) dr = N \quad (22)
\]
In analogy with the ACKS2 method, a static DFT ground state is taken as the reference to which fluctuations are considered, including the external potential \(v_0(r)\), density \(\rho_0(r)\), auxiliary potential \(u_0(r)\), and equalized chemical potential \(\mu_0\). The main difference with the original ACKS2 method, is that we now consider frequency-dependent fluctuations:
\[
v(r, \omega) = v_0(r) + \Delta v(r, \omega) \quad \rho(r, \omega) = \rho_0(r) + \Delta \rho(r, \omega)
\]
\[
u(r, \omega) = u_0(r) + \Delta u(r, \omega) \quad \mu(\omega) = \mu_0 + \Delta \mu(\omega)
\]
where \(\Delta v(r, \omega)\) is a frequency-dependent perturbation and \(\Delta \rho(r, \omega)\), \(\Delta u(r, \omega)\), and \(\Delta \mu(\omega)\) are corresponding frequency-dependent responses to the perturbation. After substitution in the Euler-Lagrange equations, one obtains
\[
\frac{\delta Q_{\text{exp}}[\rho]}{\delta \rho(r, \omega)} \bigg|_{\rho = \rho_0 + \Delta \rho} - \frac{\delta Q_{\text{exp}}[\rho]}{\delta \rho(r, \omega)} \bigg|_{\rho = \rho_0} + \Delta v(r, \omega) - \Delta u(r, \omega) = \Delta \mu(\omega) \quad (23)
\]
\[
\frac{\delta Q^o[u, N]}{\delta u(r, \omega)} \bigg|_{u = u_0 + \Delta u} - \frac{\delta Q^o[u, N]}{\delta u(r, \omega)} \bigg|_{u = u_0} - \Delta \rho(r, \omega) = 0 \quad (24)
\]
\[
\int_\Omega \Delta \rho(r, \omega) dr = 0 \quad (25)
\]
In the limit of a small perturbation, the first two equations can be linearized

$$\int \frac{\delta^2 Q^{\exp}[\rho]}{\delta \rho(r, \omega) \delta \rho(r', \omega)} \bigg|_{\rho = \rho_0} \Delta \rho(r', \omega) dr' + \Delta v(r, \omega) - \Delta u(r, \omega) \approx \Delta \mu(\omega)$$ (26)

where $f_k(r)$ and $g_n(r)$ denote density (potential) basis functions, while $C_m(\omega)$ and $U_n(\omega)$ denote the expansion coefficients of the induced density (potential) changes $\Delta \rho$ ($\Delta u$). It is worth mentioning that both basis sets are time-independent, and only the corresponding coefficients are dynamic, suggesting that the basis sets used in the ACKS2 model can also be employed herein.

D. Expansion in a finite basis

In a practical simulation, one must expand the density and the auxiliary potential fluctuations in a finite basis,

$$\Delta \rho(r, \omega) = \sum_m C_m(\omega) f_m(r)$$ (28)

$$\Delta u(r, \omega) = \sum_n U_n(\omega) g_n(r)$$ (29)

Substitution of the basis-set expansion in Eq. (26), followed by a multiplication with $f_k(r)$ and integration over $r$, leads to:

$$\sum_m \eta_{km}^{\exp}(\omega) C_m(\omega) + V_k(\omega) - \sum_n O_{kn} U_n(\omega) = \Delta \mu(\omega) D_k \quad \forall k \in \{1 \ldots M\}$$ (30)

with

$$\eta_{km}^{\exp}(\omega) = \int \int \eta^{\exp}(r, r', \omega) f_k(r) f_m(r') dr dr'$$ (31)

$$O_{kn} = \int f_k(r) g_n(r) dr$$ (32)

$$V_k(\omega) = \int f_k(r) \Delta v(r, \omega) dr$$ (33)

$$D_k = \int f_k(r) dr.$$ (34)
Similar manipulations of Eqs. (27) and (25), lead to algebraic equations as follows:

\[
\sum_{n}^{N} \chi_{kn}^{\text{imp}}(\omega)U_{n}(\omega) - \sum_{m}^{M} O_{km}C_{m}(\omega) = 0 \quad \forall k \in \{1 \ldots N\} \\
\sum_{m}^{M} D_{m}C_{m}(\omega) = 0,
\]

with

\[
\chi_{kn}^{\text{imp}}(\omega) = \int \int \chi^{\text{imp}}(r, r', \omega)g_{k}(r)g_{n}(r')drdr'.
\]

The linear system can be written in block matrix notation as follows:

\[
\begin{bmatrix}
-\eta_{M,M}^{\exp} & O_{M,N} & D_{M,1} \\
O_{N,M}^{T} & -\chi_{N,N}^{\text{imp}} & 0_{N,1} \\
D_{1,M}^{T} & 0_{1,N} & 0
\end{bmatrix}
\begin{bmatrix}
C_{M,1}(\omega) \\
U_{N,1}(\omega) \\
\Delta \mu(\omega)
\end{bmatrix} =
\begin{bmatrix}
V_{M,1}(\omega) \\
0_{N,1} \\
0
\end{bmatrix}
\]

(38)

where a bold letter denotes a block matrix and the subscript gives its dimension. For example, \(\eta_{M,M}^{\exp}\) represents the \(M \times M\) hardness submatrix, \(O_{M,N}\) is the \(M \times N\) overlap submatrix, and the 0\(_{N,1}\) (0\(_{1,N}\)) is a column (row) vector with all elements equal 0. Solving this block matrix equation gives the expansion coefficients for the induced density, i.e., \(C_{M,1}(\omega)\), which is also known as the response vector. The shape subscript will be omitted below for the sake of visual clarity.

According to linear response theory, the induced density can be expressed through an interacting response function, \(\chi\):

\[
\Delta \rho(r, \omega) = \int dr' \chi(r, r', \omega)V(r', \omega)
\]

(39)

where \(V(r, \omega)\) is the frequency-dependent external perturbation. ACKS2\(\omega\) can be used to approximate the interacting response, for which two strategies can be followed. The first and most straightforward option is to invert the block matrix in Eq. (38) directly. The top-left block of the inverse transforms the input \(V(\omega)\) into the output \(C(\omega)\), and is therefore the ACKS2\(\omega\) approximation of the interacting response.

One may also derive a useful closed expression for the interacting response matrix. This derivation starts by solving the second row of Eq. (38) to obtain \(U(\omega) = (\chi^{\text{imp}})^{\ast}O^{T}C(\omega)\). A pseudo-inverse of the implicit response matrix is needed, because it contains at least one zero eigenvalue, due to the charge distribution not being sensitive to a constant shift in Kohn-Sham potential. Next, one uses this solution to eliminate \(U(\omega)\) from the first row of Eq. (38), yielding

\[
AC(\omega) = V(\omega) - D\Delta \mu(\omega)
\]

(40)
where we introduced a shorthand $A = -\eta + O(\chi^{\text{imp}})^* O^T$ to facilitate the derivation. This equation can be solved, assuming $A$ is non-singular:

$$C(\omega) = A^{-1} \left( V(\omega) - D\Delta\mu(\omega) \right)$$

(41)

When $A$ is singular, the density response is not well-defined. While we cannot exclude this possibility of $A$ being singular, we never encountered this issue in our numerical results. The Lagrange multiplier is found by substituting this result in the third row of Eq. (38):

$$\Delta\mu(\omega) = \frac{D^T A^{-1} V(\omega)}{D^T A^{-1} D}$$

(42)

The final expression for the interacting response is:

$$C(\omega) = \chi V(\omega) = \left( A^{-1} - \frac{A^{-1} D D^T A^{-1}}{D^T A^{-1} D} \right) V(\omega)$$

(43)

The second term in $\chi$ (due to normalization) is responsible for a proper zero eigenvalue in the interacting response, which also guarantees the constraint of particle conservation, i.e., $D^T \chi = 0$.

Note that $C(\omega) = \chi V(\omega)$ does not contain an overlap matrix, unlike $O^T C(\omega) = \chi^{\text{imp}} U(\omega)$, because $V(\omega)$ is defined with respect to the density basis $f_n$, whereas $U(\omega)$ is expanded in terms of $g_n$. Hence, $\chi$ is the interacting response expanded in the density basis. If desired, one may also express it in the potential basis by assuming that perturbations in the external potential have the following form:

$$\Delta v(r, \omega) = \sum_n V'_n(\omega) g_n(r)$$

(44)

The new expansion coefficients, $V'_n(\omega)$, can always be transformed to those from Eq. (33):

$$V_k(\omega) = \sum_n O_{kn} V'_n(\omega)$$

(45)

With that, one can left-multiply Eq. (43) with $O^T$ and substitute $V(\omega)$ with $OV'(\omega)$:

$$O^T C(\omega) = O^T \chi O V'(\omega) = O^T \left( A^{-1} - \frac{A^{-1} D D^T A^{-1}}{D^T A^{-1} D} \right) O V'(\omega) = \chi' V'(\omega)$$

(46)

where $\chi'$ is finally identified as the interacting response matrix in the potential basis.

E. ACKS2$\omega$ matrix elements

So far, the precise forms of the implicit and explicit functionals were not specified, and one may use, in principle, any definition whose sum equals (or approximates) the total quasi-energy.
In this section, we show that for Kohn-Sham DFT, a convenient choice can be made, leading to straightforward equations for all coefficients in the ACKS2ω equations.

The Kohn-Sham DFT expression of the quasi-energy is

\[ Q^0[\rho] = T_s[\rho] + V[\rho] + J[\rho] + Q_{xc}[\rho] - S_s[\rho] \]  \hspace{1cm} \text{(47)}

where, \( T_s[\rho] \) and \( S_s[\rho] \) are defined using the determinant of the non-interacting system \( |\tilde{0}_s\rangle \):

\[ T_s[\rho] = \{ \langle \tilde{0}_s | \hat{T} | \tilde{0}_s \rangle \} \] \hspace{1cm} \text{(48)}

\[ S_s[\rho] = \{ \langle \tilde{0}_s | i \frac{\partial}{\partial t} | \tilde{0}_s \rangle \} \] \hspace{1cm} \text{(49)}

The quasi-energy xc functional is thereby defined as

\[ Q_{xc}[\rho] = Q_{ncl}[\rho] + (T[\rho] - T_s[\rho]) + (S[\rho] - S_s[\rho]) \] \hspace{1cm} \text{(50)}

Within the quasi-energy formalism, we employ the adiabatic approximation by replacing \( Q_{xc}[\rho] \) with a time-independent counterpart \( \{ E_{xc}[\rho] \} \).

With a semi-local xc functional, the explicit part of the energy functional in Kohn-Sham DFT takes the following form:

\[ Q^{\exp}[\rho] = \left\{ \frac{1}{2} \int \int \frac{\rho(r,t)\rho(r',t)}{|r-r'|} dr dr' + E_{xc}[\rho] \right\} \] \hspace{1cm} \text{(51)}

where the first term is the Hartree quasi-energy, \( J[\rho] \), while the second is the xc functional. The auxiliary wavefunction \( \Phi \) is a single Slater determinant of Kohn-Sham orbitals, and \( W[\Phi] \) is the Kohn-Sham kinetic energy minus functional \( S_s[\rho] \)

\[ W[\Phi] = \left\{ \sum_{i \in \text{Occ.}} \int \phi_i^*(r,t) \left( -\frac{1}{2} \nabla^2 \right) \phi_i(r,t) dr \right\} - S_s[\rho] \] \hspace{1cm} \text{(52)}

where, \( \phi_i \) is the \( i \)-th occupied (Occ.) molecular spatial orbital.

The expressions for the explicit hardness matrix and implicit response matrix with the Lehmann representation \(^{56,57}\) take the following forms in frequency space, respectively:

\[ \eta_{km}^{\exp} = \int \int \left( \frac{1}{r-r'} + \frac{\delta^2 E_{xc}[\rho]}{\delta \rho(r) \delta \rho(r')} \right) f_k(r)f_m(r') dr dr' \] \hspace{1cm} \text{(53)}

\[ \chi_{km}^{\exp}(\omega) = \lim_{\eta \to 0^+} \sum_{i \in \text{Occ.}} \sum_{a \in \text{Vir.}} (n_i - n_a) \left[ \frac{\phi_i^*(r)g_k(r)\phi_a(r)\phi_i(r')g_n(r')\phi_a^*(r')dr'}{\omega - (\varepsilon_a - \varepsilon_i) + i\eta} \right. \] \hspace{1cm} \text{(54)}
where, \( n_i \) and \( n_a \) are 1 and 0 for occupied and virtual (Vir.) molecular spatial orbitals, respectively. After simple manipulations, the matrix elements of \( \chi^{\text{imp}} \) have a simplified form

\[
\chi_{kn}(\omega) = \lim_{\eta \to 0^+} \frac{2\Omega_{ia}}{\eta} \sum_{i \in \text{Occ.}} \sum_{a \in \text{Vir.}} \langle \phi_i | g_k | \phi_a \rangle \langle \phi_a | g_n | \phi_i \rangle.
\]

(55)

where \( \Omega_{ia} = \varepsilon_a - \varepsilon_i \) and the Dirac notation is used. For closed-shell molecules, a factor four is applied instead of two in Eq. (55) and the sum is restricted to spin-up orbitals only.

**F. Dynamic polarizability and related properties**

The dynamic linear-response properties, such as dipole polarizabilities, can be derived from the frequency-dependent response matrix. Moreover, with a proper choice of density and potential basis functions, distributed polarizabilities\(^{90}\) are also available.

The potential basis set is constructed as

\[
g_n(a,\ell,m)(r) = w_a(r)R^{m}_{\ell}(r-R_a)
\]

(56)

where \( R^{m}_{\ell}(r-R_a) \) is a real solid harmonic with angular quantum number \( \ell \) and magnetic quantum number \( m \), using the position of nucleus \( a \) as origin. The functions \( w_a(r) \) \((0 \leq w_a(r) \leq 1)\) are so-called atom-in-molecule (AIM) weights functions, determining which proportion of the molecular ground-state density is assigned to atom \( a \).\(^{91}\) The rationale is that the integral of the product of such a potential basis function and a (response) density can be interpreted as distributed multipole moment.

The density basis set can be organized similarly, using atom-centered functions with unit monopole, dipole, etc. moments. One may use Gaussian basis sets,\(^{45}\) or construct a basis that is bi-orthogonal to the potential basis set,\(^{43}\) which is also the approach followed in this work.

Both basis sets are truncated by discarding all solid harmonics for which \( \ell > \ell_{\text{max}} \), where \( \ell_{\text{max}} \) is a user-specified threshold. For instance, \( \ell_{\text{max}} = 0 \) and \( \ell_{\text{max}} = 1 \) corresponds to fluctuating charges only and charges+dipoles, respectively. The total basis size is therefore \( 2(\ell_{\text{max}} + 1)^2 \) times the number of atoms.

For the remainder of this section, it is convenient to change the index notation and introduce a compound index \( t \) (or \( u \)) for the components of multipole moments, instead of separate indices \( \ell \) and \( m \). With these, we can define a distributed polarizability as:

\[
\alpha_{tu}^{ab} = -\chi_{k(a,t)n(b,u)}
\]

(57)
where $\chi_{k(a,t)n(b,u)}$ are elements of the response matrix defined in Eq. (43). When considering the case $\ell_{\text{max}} = 1$, distributed polarizability comprises several physically distinct blocks: the distributed charge-flow, $\alpha^{ab}_{qq}$, charge-dipole, $\alpha^{ab}_{q\beta}$, dipole-charge, $\alpha^{ab}_{\alpha q}$, and dipole-dipole, $\alpha^{ab}_{\alpha \beta}$, components. The subscript $q$ is used to denote the monopole block and $\alpha(\beta)$ refers to dipole blocks, whereby both $\alpha$ and $\beta$ could be $x, y, \text{ or } z$. The total molecular dipole polarizability can be recovered as follows: 

$$\alpha_{\alpha \beta} = \sum_{a,b} r^{a}_\alpha \alpha^{ab}_{qq} r^{b}_\beta + r^{a}_\alpha \alpha^{ab}_{q\beta} + \alpha^{ab}_{\alpha q} r^{b}_\beta + \alpha^{ab}_{\alpha \beta} \quad (58)$$

where $r^{a}_\alpha$ and $r^{b}_\beta$ are corresponding atomic coordinates. The isotropic dipole polarizability of molecules is formally given as:

$$\overline{\alpha} = \frac{1}{3}(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (59)$$

Eqs. (58)–(59) remain valid for frequency-dependent polarizabilities. When a real frequency is used, $\overline{\alpha}$ becomes complex (when $i\eta \neq 0$). The dipole strength function $S(\omega)$ can be computed using the imaginary part of $\overline{\alpha}$ with:

$$S(\omega) = \frac{2\omega \pi \bar{h}^2}{3} [\overline{\alpha}(\omega)]. \quad (60)$$

The excitation energies are thus determined from the positions of the peaks, and the area under the peaks represents the oscillator strength of the corresponding transition. In addition, the isotropic $C_6$ dispersion coefficient can be computed with imaginary frequencies ($\omega = iu$) using Casimir-Polder equation:

$$C_6 = \frac{3}{\pi} \int_0^{\infty} \overline{\alpha}^A(iu) \overline{\alpha}^B(iu) du, \quad (61)$$

where, superscripts $A$ and $B$ denote different molecules.

### G. Two-site ACKS2ω model

Before studying the absorption spectra of molecular systems, it is instructive to start with a simple model system to illustrate the workings of the ACKS2ω approach in analogy to the TDDFT method. We consider a two-site system of an electric dipole along $x$-axis with coordinates of -1 and 1, and only s-type density and potential functions are considered. The two-site ACKS2ω problem can be solved analytically after making the following assumptions:
1. The hardness matrix $\eta$ is
\[
\begin{pmatrix}
a & b \\
b & a
\end{pmatrix}
\] where non-negative numbers $a$ and $b$ denotes atomic hardness and the classical Coulomb interaction between the density functions, respectively. The $xc$ contribution to the hardness is neglected entirely, i.e., the RPA is used.

2. The overlap matrix is
\[
\begin{pmatrix}
c & 0 \\
0 & c
\end{pmatrix}
\] where $c$ is the overlap between the potential and density functions on the same site. Any overlap between functions on different sites is neglected for simplicity. Furthermore, we assume that the density basis functions are normalized, i.e. $D_k = 1$ for all $k$ in Eq. (34).

3. The non-interacting response matrix is
\[
\begin{pmatrix}
f & -f \\
-f & f
\end{pmatrix}
\] with
\[
f = \frac{2\Omega d}{(\omega + i\eta)^2 - \Omega^2}
\] (62)
where $\Omega_{12}$ is the excitation energy between the ground state and the first excited state, determining the pole position of the non-interacting response function. In addition, an arbitrary amplifier $d$ is added to create a more general non-interacting response matrix.

One may solve the interacting response of this model analytically, by working out Eq. (43). Doing so leads to an interacting response matrix of the form
\[
\begin{pmatrix}
g & -g \\
-g & g
\end{pmatrix}
\] with
\[
g = \frac{2\Omega d}{[(\omega + i\eta)^2 - \Omega^2]c^2 - 4\Omega(a - b)d}
\] (63)
Therefore, the pole of the interacting response function is
\[
\omega = \sqrt{\Omega^2 + \frac{4\Omega(a - b)d}{c^2}} > \Omega
\] (64)
where the condition $a > b$ is generally satisfied with the RPA approximation, because the Hartree kernel is positive definite. This inequality implies that the pole of the interacting response is shifted to higher frequencies compared to the non-interacting response, when using RPA.

Figure 1 gives the absorption spectra computed by both non-interacting and interacting response functions, where the parameters $a, b, c, d, \Omega, \eta$ are assigned 1.0, 0.2, 3.0, 1.2, 1.2, and 0.05 (all in atomic units), respectively. The position of the pole is depicted with dotted (dashed) lines for the interacting (non-interacting) response function, overlapping with the peak position in
the corresponding absorption spectrum. It can be seen that the pole of the interacting response function shifts to a higher frequency compared to the non-interacting case.

FIG. 1. Spectra of a finite dipole along x-axis with a single excited state. The pole of the non-interacting (interacting) system is indicated by a dotted (dashed) line. Numerical parameters are given in the main text.

III. COMPUTATIONAL DETAILS

This section presents the details of the numerical validation of ACKS2ω using the TS42 database and its TS27 subset. As discussed in Section II D, both potential and density basis functions are frequency-independent. Here, the basis sets are constructed in the same way as in one of our previous works on ACKS2⁴³. The MBIS method⁹⁴ was used to define the AIM weight functions, \( w_a(r) \). Using the same procedure as in Ref. 43, the density basis set consists of non-interacting responses to each potential basis function, when used as a perturbation. This set is augmented with one Fukui function, to have at least one basis function that is not norm-preserving. Later, a linear transformation is applied to the density basis functions, such that they become bi-orthogonal to the potential basis, enabling one to label them as s-type, p-type, etc. This definition of the density basis set is relatively expensive, and is geared towards an accurate description of linear response functions. The goal of this work is to test the validity of the ACKS2ω theory, justifying the use of carefully constructed basis functions. The bi-orthogonality of the density and potential basis functions also simplifies the elements of ACKS2ω working
matrix in Eq. (38). More specifically, the overlap matrix $O$ becomes an identity matrix, and all non-zero elements of the vector $D$ are equal to 1, corresponding to integrals from s-type density functions. Moreover, when the adiabatic approximation is used, the hardness matrix becomes frequency-independent and takes the same form as in the ACKS2 paper. More specifically, integrals including the hardness kernel of the explicit functional were evaluated numerically using a pruned Becke-Lebedev integration grid. Integrals over the Hartree kernel were implemented with a Becke-Poisson solver. Although the analytic expressions for LDA and PBE kernels are already provided in LibXC, integrals involving the exchange-correlation kernel were evaluated with the finite difference method used to be consistent with the previous work. The only frequency-dependent parameters of ACKS2 are found in the non-interacting response tensor, which can be evaluated using Eq. (54) on the same numerical grids.

The workflow of the ACKS2 parameterization in this work is analogous to our earlier assessment of the ACKS2 theory:

1. The molecular structures listed in the T42 data set are optimized using DFT at B3LYP/aug-cc-pVDZ level. (The optimized geometries are available in the Supplementary Material.)

2. A new DFT calculation with LDA or PBE functional is employed to obtain ground-state information used in ACKS2 parameter evaluations, e.g., unperturbed electron density and Kohn-Sham orbitals. All DFT calculations were performed in the quantum chemistry program GAUSSIAN16.

3. The Kohn-Sham density and orbitals are then imported into ACKS2 implemented in the Horton library, where the MIBS partitioning scheme is applied to generate the weight function $w_a(r)$ for each atom. In ACKS2, all parameters are evaluated on numerical Becke-Lebedev grids implemented in Horton, providing six user options from cheap to expensive: coarse, medium, fine, veryfine, ultrafine, and insane. medium grids are employed for all ACKS2 calculations, unless noted elsewhere.

4. Frequency-dependent distributed polarizabilities are evaluated up to charges ($\ell_{\text{max}} = 0$) and charges+dipoles ($\ell_{\text{max}} = 1$), respectively. An LDA or PBE hardness kernel is used, consistently with the functional in step (2).

5. Consequently, dynamic dipole polarizabilities can be constructed using the distributed polarizabilities from Eq. (58).
To demonstrate the accuracy of ACKS2ω on dynamic linear-response properties, we first studied absorption spectra of 42 molecules from the TS42 data set. We only estimate the absorption spectra at the PBE/aug-cc-pVDZ level to save computational resources. 300 real frequencies ranging from 0.2 to 0.5 a.u. (i.e., 5.4–13.6 eV) are selected for absorption spectra, and the parameter \( \eta \) in Eq. (54) is set to 0.001. Then, the isotropic \( C_6 \) coefficients (in a.u.) are investigated for 903 molecular pairs constructed from the 42 molecules. The effect of xc functional is investigated on the \( C_6 \) coefficient by comparing two types of functional, i.e., LDA and PBE. The Slater exchange functional and the VWN5 correlation functional are used for the LDA functional in this work. Moreover, four different Dunning basis sets, aug-cc-pVDZ, aug-cc-pVTZ, d-aug-cc-pVDZ, and d-aug-cc-pVTZ, are utilized to study the impact of the basis size. The integral in Eq. (61) is evaluated using the Gaussian-Legendre quadrature with 12 imaginary frequencies. Furthermore, for comparison, we also evaluated the linear-response properties using linear-response TDDFT (LrTDDFT) with the LDA (PBE) functional, referred to as LrTDLDA (LrTDPBE). All LrTDDFT calculations are carried out in the quantum chemistry program Dalton.

In the following context, we use the notation ACKS2ω@X to specify the ACKS2ω model with parameters estimated using functional X, for instance ACKS2ω@LDA indicates that LDA functional is used. The ACKS2ω@X evaluated with both \( \ell_{\text{max}} = 0 \) and \( \ell_{\text{max}} = 1 \) are called s-type and sp-type ACKS2ω@X, respectively. As an exception to this nomenclature, ACKS2ω@LDAx means that the ground-state DFT uses full LDA xc functional, just as ACKS2ω@LDA, but that the correlation contribution to the hardness kernel is neglected. (Only Hartree and exchange are included.)

In this work, all parameters in ACKS2ω are computed as expectation values of an electronic wavefunction, which is the most time-consuming step. For applications of ACKS2ω to larger systems, this step should be replaced by a simpler empirical model for the ACKS2ω, analogous to general PFFs, such that the calculation of all matrix elements becomes fast, with a quadratic complexity with the number of atoms in the system. In the long run, we hope that screening approximations and advanced Poisson solvers may further reduce the scaling of setting up and solving the relevant part of the equations to \( O(N_{\text{atom}} \log N_{\text{atom}}) \).

In comparison, the bottleneck of TDDFT is the transformation of electron repulsion integrals (ERI) from atomic orbitals (AO) to molecular orbitals (MO), which cannot be applied in large-scale systems due to its significantly expensive \( O(N_{\text{occ}} N_{\text{AO}}^4) \) complexity from the conventional transformation or \( O(N_{\text{occ}}^2 N_{\text{vir}}^2 N_{\text{aux}}) \) from density fitting procedures where \( N_{\text{AO}} \) is the size of the
basis set and \( N_{\text{occ}} \), \( N_{\text{vir}} \) and \( N_{\text{aux}} \approx 3N_{\text{AO}} \) are the number of occupied, virtual orbitals and the size of auxiliary basis sets, respectively.\(^{107-110}\)

Finally, for the matrix inversion to calculate the interacting response matrix, a similar linear-algebra technology can be employed for both ACKS2\( \omega \) and TDDFT with a semi-local exchange-correlation functional. However, the dimension of ACKS2\( \omega \) working matrix with \( l_{\text{max}} = 1 \) is \( 4N_{\text{atom}} \), in practice much less than the TDDFT counterpart, i.e., \( N_{\text{occ}} \times N_{\text{vir}} \).

Because our current implementation is merely a prototype, we only illustrate timings of the different steps in the computational workflow, for the case of benzene with an Aug-cc-pVTZ basis set, on a 4-core AMD EPYC 7552 processor (AMD Zen2 microarchitecture). The following numbers may change with future software and hardware improvements. The calculation of the hardness matrix and 13 (twelve frequency-dependent and one static) Kohn-Sham response matrices take 101 s in this case. Once the matrix elements are available, the ACKS2\( \omega \)@LDA response calculation is trivial and has a much lower runtime (1.97 ms) compared to the corresponding LrT-DLDA calculation (290 s), excluding the walltime of ground-state DFT and ERI transformation.

\section*{IV. RESULTS AND DISCUSSION}

\subsection{Absorption spectra of molecules in the TS42 set}

Figure. 2 shows the results computed by sp-type ACKS2\( \omega \) for four example molecules, i.e., \( \text{C}_2\text{H}_2 \), \( \text{C}_2\text{H}_4 \), \( \text{C}_2\text{H}_5\text{OH} \) and \( \text{C}_2\text{H}_6 \), while the other spectra can be found in Figures S1-S5 of the Supplementary Material. From the figures, we can see that the position of peaks obtained by the ACKS2\( \omega \) model overlaps almost perfectly with the LrTDPBE data, suggesting that the ACKS2\( \omega \) model is a faithful approximation of its TDDFT reference. At higher excitation energies, beyond 13.6 eV, we observe a similar correspondence of the spectra, which is not included in the figures for the sake of visual clarity. It should be noted that a near-quantitative reproduction of the reference can be achieved with the sp-type basis functions only, i.e., charges+dipoles functions, which agrees well with the ACKS2 model.\(^{43}\) The small deviation between ACKS2\( \omega \) and TDDFT is potentially due to the atom-condensed basis functions and the numerical integration errors in the calculation of the parameters.
FIG. 2. Comparison of optical absorption spectra, computed with sp-type ACKS2ω@PBE and LrTDPBE methods for C$_2$H$_2$, C$_6$H$_4$, C$_2$H$_5$OH and C$_2$H$_6$ molecules, using the aug-cc-pVDZ basis set in the DFT calculations.

B. Comparison of ACKS2ω and TDDFT $C_6$ coefficients

This section presents a comparison of $C_6$ coefficients obtained with ACKS2ω and TDDFT, to validate the ACKS2ω formalism. Figure 3 shows a parity plot of $C_6$ dispersion coefficients for 903 molecular pairs, based on the TS42 data set, computed with s-type and sp-type ACKS2ω models. The ACKS2ω parameters are derived from LDA/aug-cc-pVDZ calculations and LrTDLDA/aug-cc-pVDZ $C_6$ coefficients are used as a reference. All s-type ACKS2ω parametrizations significantly underestimate $C_6$ coefficients, averaging around 93% with respect to the reference values. The reason for this large error is that the dipole polarizability is significantly underestimated due
to less complete basis sets in s-type ACKS2. This effect is amplified in the isotropic $C_6$ coefficient, because it scales quadratically with the dipole polarizability. In contrast, very small errors can already be obtained with the sp-type ACKS2@LDA model, i.e. just considering fluctuating atomic charges and dipoles.

Table I presents the mean percentage errors (MPE) and mean absolute percentage errors (MAPE) over all molecule pairs, between LrTDLDA reference values and sp-type ACKS2@LDA models, for different orbital basis sets. For all tested basis sets, the sp-type ACKS2@LDA has a negative MPE, indicating that ACKS2@LDA slightly underestimates $C_6$ with respect to the TDDFT reference. Moreover, in all cases, sp-type ACKS2@LDA has a MAPE below 3%, which numerically confirms the validity of ACKS2@LDA and its ability to construct faithful approximations of its TDDFT reference. The absolute value of the MPE is clearly smaller than the MAPE, suggesting that the underestimation of $C_6$ by ACKS2@LDA is not systematic. Overall, the MPE and MAPE are not sensitive to the orbital basis, safe for a slight increase in error for larger orbital basis sets. This is to be expected, since the TDDFT calculations with larger basis sets have richer response functions, which are harder to reproduce with a simple sp-type ACKS2@LDA model.

| Basis sets  | MPE (%) | MAPE (%) |
|-------------|---------|----------|
| aug-cc-pVDZ | -1.62   | 2.35     |
| aug-cc-pVTZ | -1.94   | 2.60     |
| d-aug-cc-pVDZ | -1.41  | 2.31     |
| d-aug-cc-pVTZ | -1.81  | 2.55     |

The non-zero MPEs and MAPEs in table I are due to the finite sp basis used in ACKS2@LDA. This is unavoidably a smaller basis compared to the TDDFT reference calculations, in which the Casida equations are solved in the product space of the occupied and virtual Kohn-Sham orbitals. One may reduce the error of ACKS2@LDA by systematically including higher-order atomic multipoles, shown in table II. It should be noted that very fine numerical grids were needed to obtain numerically stable results for higher values of $\ell_{\text{max}}$. This also results in a small deviation from $\ell_{\text{max}} = 1$.
FIG. 3. Parity plot of the $C_6$ coefficients (in a.u.) of all 903 molecular dimers computed by ACKS2$\omega$@LDA compared to the LrTDLDA reference values. Two datasets are included: the lowest set (blue) is generated by s-type ACKS2$\omega$@LDA (see text), while the higher set (red) is generated by sp-type ACKS2$\omega$@LDA. The first bisector is plotted as a solid black line, and a dashed line parallel to the bisector (factor 0.07 lower) is representative of the MAPE of the s-type ACKS2$\omega$ model.

compared to table I, for which medium grids were used. Increasing $\ell_{\text{max}}$ beyond 4 is expected to lower the MAPE even further, provided that even larger integration grids are used, and in the limit of a complete basis set, we expect the MAPE to vanish. The near zero ($-4.88 \times 10^{-4}\%$) MPE obtained with monopoles and dipoles is likely coincidental, as the MPE is higher for $\ell_{\text{max}} > 1$.

C. Comparison to experimental $C_6$ coefficients

Figure 4 shows the MPE and MAPE of $C_6$ coefficients computed by ACKS2$\omega$ and LrTDLDA from experimentally-derived reference taken from Ref. 87. We only consider results computed by sp-type ACKS2$\omega$ due to the large errors made by s-type ACKS2$\omega$ discussed in Section IV B. ACKS2$\omega$ parameters were derived using different xc functionals to study the impact of the functional. Some interesting observations can be made:
TABLE II. Comparison of the performance of ACKS2ω@LDA with the aug-cc-pVDZ basis set derived using the different bi-orthogonal basis sets (defined by $\ell_{\text{max}}$, see text). MAPE (MPE) stand for the mean absolute percentage error (mean percentage error) between $C_6$ coefficients of LrTDLDA references and the corresponding ACKS2ω results for the 903 intermolecular pairs from the TS42 data set.

| $\ell_{\text{max}}$ | MAPE (%) | MPE (%)   |
|---------------------|----------|-----------|
| 0                   | 93.35    | $2.18 \times 10^{-1}$ |
| 1                   | 2.39     | $-4.88 \times 10^{-4}$ |
| 2                   | 2.12     | $1.32 \times 10^{-3}$ |
| 3                   | 1.79     | $1.27 \times 10^{-3}$ |
| 4                   | 1.59     | $3.63 \times 10^{-4}$ |

1. The positive MPE implies that all computational models in this work slightly overestimate $C_6$ values to some extent.

2. For LrTDLDA, the MPE almost equals MAPE, except when using the aug-cc-pVDZ basis. This suggests LrTDLDA systematically overestimates $C_6$ values when extensive basis sets are used. The MAPE (and MPE) increases with the size of the basis, and it is found to be converged at around 7%.

3. The MAPE (MPE) of ACKS2ω has a similar trend as LrTDLDA, but two significant differences should be pointed out. First, the ACKS2ω model has a larger MAPE than MPE, indicating that the overestimation is not systematic in the ACKS2 model, i.e., for some molecules, ACKS2ω underestimates $C_6$ coefficients. Second, ACKS2ω@LDA has a lower MAPE (MPE) than the corresponding LrTDLDA for all cases, implying that the improvement compared to LrTDDFT is somewhat systematic. One possible expansion is that TDDFT always gives an overestimated $C_6$ with LDA functional, and the incomplete basis in ACKS2ω compensates for the overestimation of TDDFT to some extent, leading to a lower MAPE. This type of error compensation is obviously fortuitous, and should therefore not be relied upon blindly.

4. The comparison between ACKS2ω@LDA and ACKS2ω@PBE shows a systematic improvement when using PBE instead of LDA. One possible reason could be that the contribution of correlation functional can be described more precisely with PBE than LDA.
inspired us to also test the ACKS2ω@LDAx model, which entirely ignores the correlation contribution in the hardness kernel, compared to ACKS2ω@LDA. As expected, it shows a significant deviation from the ACKS2ω@LDA model. Interestingly, ACKS2ω@LDAx performs slightly better than ACKS2ω@PBE, except for the aug-cc-pVDZ basis, where the latter has a lower MAPE (3.84%). Besides the potentially beneficial error compensation, these results also show that ACKS2ω is quite sensitive to the choice of functional, because the TDDFT reference also exhibits this sensitivity.

![Graph](image-url)

**FIG. 4.** The impact of the size of the basis set on the error of different methods with respect to experimental reference data: (a) MPE and (b) MAPE, where ‘aDZ’, ‘aTZ’, ‘daDZ’, and ‘daTZ’ denote aug-cc-pVDZ, aug-cc-pVTZ, d-aug-cc-pVDZ, and d-aug-cc-pVTZ basis sets, respectively.

**D. Comparison of ACKS2ω and range-separated TDDFT C6 coefficients**

Toulouse *et al.* calculated C6 coefficients using range-separated hybrid TDDFT at the LDA/d-aug-cc-pVTZ level (TDRSHELDA) for 27 homodimers from the TS27 data set. The spirit of the TDRSHELDA method is to improve the quality of exchange kernel in TDDFT, by incorporating Hartree-Fock exchange at longer ranges, thereby suppressing systematic errors of pure exchange functionals. Table III reports the results of C6 coefficients computed by the ACKS2ω model.
for the TS27 data set, where effects of different Hartree-exchange-correlation kernels are also presented. The literature results for TDRSHLDA\textsuperscript{88} and experimental data\textsuperscript{87} are also presented. We use a similar notation as Ref. 88, e.g., the bare LDA indicates no hardness kernel is applied, while RPA@LDA, TDLDAx, and TDLDA mean that the response kernel is evaluated considering only Hartree, Hartree + LDA exchange, and whole LDA Hartree-exchange-correlation kernel, respectively. Corresponding results with PBE functional are also reported.

As we can see from Table III, bare LDA and PBE largely overestimate the $C_6$ coefficients by as much as 138.96\% and 134.92\%, respectively, as one could expect.\textsuperscript{88} However, RPA@LDA and RPA@PBE, by making use of the Hartree kernel only, underestimate the coefficients by 12.64\% and 13.59\%, respectively. LDAx, LDA, and PBE give $C_6$ coefficients with overall comparable accuracy, LDAx having a slightly smaller MAPE of 5.29\% in comparison to the MAPE of LDA and PBE, 6.18\% and 5.38\%, respectively. The MAPE of ACKS2ω@LDAx is lower than LrT-DLDA (6.3\%),\textsuperscript{88} but greater than TDRSHLDA (5.17\%),\textsuperscript{88} demonstrating that when correlation is entirely ignored in response calculations, ACKS2ω@LDAx gives a better performance, close to the TDRSHLDA method. Note that ACKS2ω@LDAx has a positive MPE but TDRSHLDA negative, indicating that $C_6$ coefficients obtained by ACKS2ω@LDAx and TDRSHLDA are in general overestimated and underestimated, respectively. As discussed above, LrTDLDA overestimates $C_6$ coefficients and ACKS2ω@LDA slightly compensates for the overestimation due to the less complete bio-orthogonal basis sets. However, the compensation is too small to offer a significant improvement compared to TDRSHLDA. Interestingly, the results are improved and even better than PBE by removing the electron correlation contribution in response calculations, which again demonstrates that the effects of xc functional on $C_6$ coefficients with ACKS2ω are of significant importance.

V. CONCLUSIONS AND OUTLOOK

A frequency-dependent ACKS2 model, referred to as ACKS2ω, is proposed using the quasi-energy formalism. This allows us to approach ACKS2ω directly using the variational principle, in the same way as the time-independent ACKS2 derivation. For the xc contribution to the hardness, an adiabatic approximation is applied, and the hardness is thereby frequency-independent, just as in the ACKS2 model. For the frequency-dependent non-interacting response matrix, a similar Lehmann representation is employed as in the static case. Given the hardness and non-interacting
TABLE III. Isotropic $C_6$ coefficients (in a.u.) for the TS27 data set obtained by the ACKS2ω model with bare LDA, RPA@LDA, LDAx, LDA, PBE, RPA@PBE, and PBE kernels, with d-aug-cc-pVTZ basis sets. Computational values of TDRSHLDA$^{88}$ are presented, as well as the experimental reference data compiled from Ref. 87. The geometry was optimized at the B3LYP/aug-cc-pVDZ level. Mean percentage error (MPE) and mean absolute percentage errors (MAPE) over all molecules with respect to reference values are given.

|            | ACKS2ω | TDRSHLDA$^a$ | Exp.$^b$ |
|------------|--------|-------------|---------|
|            | Bare LDA | RPA@LDA | LDAx | LDA | Bare PBE | RPA@PBE | PBE |         |         |
| H$_2$      | 20.11   | 11.01     | 14.03 | 14.45 | 18.88 | 10.41 | 13.65 | 12.70 | 12.10 |
| HF         | 32.94   | 19.14     | 22.20 | 22.58 | 33.17 | 19.29 | 22.65 | 19.20 | 19.00 |
| H$_2$O     | 84.09   | 43.17     | 51.07 | 52.09 | 83.95 | 43.17 | 51.92 | 43.40 | 45.30 |
| N$_2$      | 179.25  | 63.11     | 72.21 | 75.16 | 178.47 | 63.16 | 73.22 | 72.70 | 73.30 |
| CO         | 182.42  | 65.87     | 76.60 | 77.73 | 180.90 | 65.88 | 77.91 | 77.10 | 81.40 |
| NH$_3$     | 166.17  | 79.17     | 94.82 | 96.88 | 163.92 | 78.34 | 95.78 | 72.70 | 73.30 |
| CH$_4$     | 241.97  | 111.97    | 134.34 | 137.05 | 234.09 | 109.11 | 134.05 | 121.20 | 129.70 |
| CH$_3$OH   | 314.90  | 128.76    | 150.73 | 153.25 | 311.55 | 128.13 | 152.87 | 138.40 | 165.20 |
| CH$_3$CO   | 581.17  | 156.22    | 175.71 | 177.72 | 578.60 | 156.75 | 178.37 | 179.80 | 184.90 |
| N$_2$O     | 497.75  | 180.45    | 212.02 | 216.01 | 494.75 | 180.27 | 216.33 | 198.90 | 204.10 |
| HBr        | 524.77  | 182.43    | 216.97 | 221.24 | 520.74 | 181.76 | 221.56 | 205.50 | 216.60 |
| H$_2$S     | 543.41  | 182.32    | 219.14 | 223.72 | 529.72 | 178.96 | 220.21 | 209.00 | 216.80 |
| CH$_3$OH   | 426.69  | 196.89    | 231.62 | 235.60 | 418.51 | 194.35 | 233.70 | 205.00 | 222.00 |
| SO$_2$     | 961.52  | 263.01    | 298.19 | 301.89 | 960.93 | 264.22 | 304.05 | 295.30 | 294.00 |
| C$_2$H$_4$ | 651.83  | 259.34    | 307.48 | 313.29 | 640.10 | 256.29 | 311.24 | 287.30 | 300.20 |
| CH$_3$NH$_2$ | 601.55 | 271.57    | 320.30 | 326.20 | 588.09 | 267.27 | 322.48 | 279.60 | 303.80 |
| SiH$_4$    | 777.20  | 302.19    | 369.60 | 378.07 | 725.68 | 288.91 | 364.81 | 329.60 | 343.90 |
| C$_2$H$_6$ | 750.74  | 332.35    | 392.56 | 399.72 | 727.40 | 324.66 | 392.87 | 352.70 | 381.90 |
| Cl$_2$     | 1095.68 | 315.22    | 366.12 | 371.26 | 1077.08 | 312.46 | 369.93 | 385.40 | 389.20 |
| CH$_3$CHO  | 923.40  | 375.91    | 434.97 | 441.78 | 904.54 | 371.51 | 438.12 | 386.60 | 401.70 |
| COS        | 1415.93 | 358.36    | 409.47 | 415.10 | 1399.21 | 357.42 | 415.24 | 425.40 | 402.20 |
| CH$_3$OCH$_3$ | 1091.09 | 485.48    | 566.65 | 576.14 | 1061.04 | 476.27 | 568.58 | 496.10 | 534.10 |
| C$_3$H$_6$ | 1461.23 | 583.62    | 683.18 | 694.79 | 1423.72 | 573.31 | 686.75 | 622.00 | 662.10 |
| CS$_2$     | 3759.03 | 733.53    | 841.33 | 852.85 | 3710.36 | 730.39 | 852.50 | 923.00 | 871.10 |
| CCl$_4$    | 5918.94 | 1723.00   | 1949.94 | 1971.80 | 5787.63 | 1703.58 | 1962.53 | 1924.90 | 2024.10 |
| MPE        | 138.96  | -12.64    | 2.42 | 4.20 | 134.92 | -13.59 | 3.32 | -3.83 |
| MAPE       | 138.96  | 12.69     | 5.29 | 6.18 | 134.92 | 13.70 | 5.38 | 5.17 |

$^a$ From Ref. 88, computed by range-separated hybrid TDDFT at the LDA/d-aug-cc-pVTZ level.

$^b$ From Ref. 87, obtained from experimental dipole oscillator strength distribution data.
response matrix, the interacting response matrix can be reproduced in analogy to the procedure used in the ACKS2 model.

The ACKS2ω equations are validated with several numerical assessments. Absorption spectra obtained from the strength function are evaluated for all 42 molecular monomers from the TS42 data set. The results agree well with the LrTDDFT reference data, indicating that the ACKS2ω model is reasonably accurate for linear-response property calculations of finite systems. Furthermore, we test $C_6$ coefficients for the TS42 data set to validate the new model, including 903 organic and inorganic molecule pairs. These tests confirm that ACKS2ω can reproduce TDDFT $C_6$ coefficients with only a small systematic error, when at least fluctuating atomic charges and dipoles are used.

A comparison of ACKS2ω, using the LDA and PBE kernels, to experimental data and results obtained with range-separated calculations, provides some additional insights. The deviation of the ACKS2ω $C_6$ coefficients from the experiment is quite sensitive to the choice of the functional, with PBE and LDAx (correlation omitted from the hardness kernel), being favorable choices. The best ACKS2ω model, ACKS2ω@PBE with the aug-cc-pVDZ basis, gives $C_6$ coefficients of molecules with an MAPE of 3.84%, a slight improvement over the TS method (6.3%). This improvement is significant because it potentially provides a better way to describe non-local dispersion energy between molecular dimers, which is a topic of ongoing research. In addition, the ACKS2ω@LDAx model has only a slightly inferior accuracy of $C_6$ coefficients than TDRSHLDA response calculations, with MAPEs of 5.29% and 5.17%, respectively, for 27 homodimers from the TS27 database.

The strength of the ACKS2ω model is that, once parameterized, calculations involving response kernels have a low computational cost, comparable in complexity to conventional polarizable force fields. In this work, the parametrization is relatively expensive to obtain accurate predictions, thereby showing that ACKS2ω is capable of reproducing its LrTDDFT reference. In future work, simpler force-field like parametrizations could be used instead, to overcome the computational bottleneck of the current parametrization. We anticipate that this approach will be beneficial, e.g. for calculations of long-range correlation energies or optical properties of extended systems, for which DFT would be infeasible.
SUPPLEMENTARY MATERIAL

Additional display items showing spectra for the remaining molecules of the TS42 set, not included in Fig. 2 are included in a Supplementary PDF file. Optimized geometries for the TS42 molecules are stored in XYZ format in a Supplementary ZIP file.

ACKNOWLEDGMENTS

Y.C. and T.V. acknowledge the Foundation of Scientific Research - Flanders (FWO, file number G0A9717N) and the Research Board of Ghent University (BOF) for their financial support. The resources and services used in this work were provided by the VSC (Flemish Supercomputer Center), funded by the Research Foundation - Flanders (FWO) and the Flemish Government. We thank Dr. Jelle Vekeman for helpful comments on the manuscript.

DATA AVAILABILITY STATEMENT

The data that supports the findings of this study are available within the article and its supplementary material.
REFERENCES

1A. Warshel and M. Levitt, J. Mol. Biol. 103, 227 (1976).
2G. A. Kaminski, H. A. Stern, B. J. Berne, R. A. Friesner, Y. X. Cao, R. B. Murphy, R. Zhou, and T. A. Halgren, J. Comput. Chem. 23, 1515 (2002).
3P. Ren and J. W. Ponder, J. Comput. Chem. 23, 1497 (2002).
4W. L. Jorgensen, K. P. Jensen, and A. N. Alexandrova, J. Chem. Theory Comput. 3, 1987 (2007).
5Y. Shi, Z. Xia, J. Zhang, R. Best, C. Wu, J. W. Ponder, and P. Ren, J. Chem. Theory Comput. 9, 4046 (2013).
6G. Lamoureux, A. D. MacKerell, and B. Roux, J. Chem. Phys. 119, 5185 (2003).
7H. Yu, T. Hansson, and W. F. Van Gunsteren, J. Chem. Phys. 118, 221 (2003).
8J. A. Lemkul, J. Huang, B. Roux, and A. D. Mackerell, Chem. Rev. 116, 4983 (2016).
9W. J. Mortier, K. V. Genechten, and J. Gasteiger, J. Am. Chem. Soc. 107, 829 (1985).
10W. J. Mortier, S. K. Ghosh, and S. Shankar, J. Am. Chem. Soc. 108, 4315 (1986).
11C. Bai, S. Kale, and J. Herzfeld, Chem. Sci. 8, 4203 (2017).
12M. Cools-Ceuppens, J. Dambre, and T. Verstraelen, J. Chem. Theory Comput. 18, 1672 (2022), arXiv:2109.13111.
13P. J. Van Maaren and D. D. Van Spoel, J. Phys. Chem. B 105, 2618 (2001).
14A. P. E. Kunz and W. F. Van Gunsteren, J. Phys. Chem. A 113, 11570 (2009).
15S. W. Rick, S. J. Stuart, and B. J. Berne, J. Chem. Phys. 101, 6141 (1994), arXiv:9406002 [chem-ph].
16S. W. Rick and B. J. Berne, J. Am. Chem. Soc. 118, 672 (1996).
17H. A. Stern, F. Rittner, B. J. Berne, and R. A. Friesner, J. Chem. Phys. 115, 2237 (2001).
18S. Patel and C. L. Brooks, J. Comput. Chem. 25, 1 (2004).
19S. Patel, A. D. Mackerell, and C. L. Brooks, J. Comput. Chem. 25, 1504 (2004).
20A. K. Rappé and W. A. Goddard, J. Phys. Chem. 95, 3358 (1991).
21Y. Zhong and S. Patel, J. Phys. Chem. B 114, 11076 (2010).
22D. M. York and W. Yang, J. Chem. Phys. 104, 159 (1996).
23M. Devereux, S. Raghunathan, D. G. Fedorov, and M. Meuwly, J. Chem. Theory Comput. 10, 4229 (2014).
24O. T. Unke, M. Devereux, and M. Meuwly, J. Chem. Phys. 147, 10.1063/1.4993424 (2017).
M. Devereux, M. Pezzella, S. Raghunathan, and M. Meuwly, J. Chem. Theory Comput. 16, 7267 (2020).

R. T. Sanderson, Science (80-. ). 114, 670 (1951).

A. C. Van Duin, A. Strachan, S. Stewman, Q. Zhang, X. Xu, and W. A. Goddard, J. Phys. Chem. A 107, 3803 (2003).

K. S. Smirnov and D. Bougeard, Chem. Phys. 292, 53 (2003).

A. Hallil, R. Tétot, F. Berthier, I. Braems, and J. Creuze, Phys. Rev. B - Condens. Matter Mater. Phys. 73, 1 (2006).

P. Bultinck, W. Langenaeker, P. Lahorte, F. De Proft, P. Geerlings, M. Waroquier, and J. P. Tollenaere, J. Phys. Chem. A 106, 7887 (2002).

A. C. Van Duin, S. Dasgupta, F. Lorant, and W. A. Goddard, J. Phys. Chem. A 105, 9396 (2001).

P. Bultinck, R. Vanholme, P. L. Popelier, F. De Proft, and P. Geerlings, J. Phys. Chem. A 108, 10359 (2004).

Q. Yang and K. A. Sharp, J. Chem. Theory Comput. 2, 1152 (2006).

T. Verstraelen, E. Pauwels, F. De Proft, V. Van Speybroeck, P. Geerlings, and M. Waroquier, J. Chem. Theory Comput. 8, 661 (2012).

C.-M. Ionescu, S. Geidl, R. Svobodová Vařeková, and J. Koča, J. Chem. Inf. Model. 53, 2548 (2013).

R. Chelli, P. Procacci, R. Righini, and S. Califano, J. Chem. Phys. 111, 8569 (1999), number: 18.

R. a. Nistor, J. G. Polihronov, M. H. Müser, and N. J. Mosey, J. Chem. Phys. 125, 94108 (2006).

L. Warren, J. Davis, and S. Patel, J. Chem. Phys. 128, 144110 (2008).

R. Nistor and M. Müser, Phys. Rev. B 79, 104303 (2009).

T. Verstraelen, P. W. Ayers, V. Van Speybroeck, and M. Waroquier, Journal of Chemical Physics 138, 10.1063/1.4791569 (2013).

R. Chelli, M. Pagliai, P. Procacci, G. Cardini, and V. Schettino, J. Chem. Phys. 122, 10.1063/1.1851504 (2005).

J. Chen and T. J. Martínez, Chem. Phys. Lett. 438, 315 (2007).

T. Verstraelen, S. Vandenbrade, and P. W. Ayers, Journal of Chemical Physics 141, 10.1063/1.4901513 (2014).
M. M. Islam, G. Kolesov, T. Verstraelen, E. Kaxiras, and A. C. T. van Duin, J. Chem. Theory Comput. 12, 3463 (2016).

P. Gütlein, L. Lang, K. Reuter, J. Blumberger, and H. Oberhofer, Journal of Chemical Theory and Computation 15, 4516 (2019).

P. Gütlein, J. Blumberger, and H. Oberhofer, Journal of chemical theory and computation 16, 5723 (2020).

A. Stone and C.-S. Tong, Chemical Physics 137, 121 (1989).

J. F. Dobson, A. White, and A. Rubio, Phys. Rev. Lett. 96, 4 (2006).

J. Hermann, D. Alfè, and A. Tkatchenko, Nat. Commun. 8, 10.1038/ncomms14052 (2017).

K. Jackson, M. Yang, and J. Jellinek, J. Phys. Chem. C 111, 17952 (2007).

K. Jackson and J. Jellinek, J. Chem. Phys. 145, 244302 (2016).

A. J. Misquitta, J. Spencer, A. J. Stone, and A. Alavi, Phys. Rev. B - Condens. Matter Mater. Phys. 82, 1 (2010).

J. F. Dobson and T. Gould, J. Phys. Condens. Matter 24, 10.1088/0953-8984/24/7/073201 (2012).

A. J. Misquitta, R. Maezono, N. D. Drummond, A. J. Stone, and R. J. Needs, Phys. Rev. B - Condens. Matter Mater. Phys. 89, 1 (2014).

E. Runge and E. K. U. Gross, Physical Review Letters 52, 997 (1984).

C. A. Ullrich, Time-dependent density-functional theory: concepts and applications (OUP Oxford, 2011).

M. A. Marques, N. T. Maitra, F. M. Nogueira, E. K. Gross, and A. Rubio, Fundamentals of time-dependent density functional theory, Vol. 837 (Springer, 2012).

K. Burke, J. Werschnik, and E. K. Gross, J. Chem. Phys. 123, 10.1063/1.1904586 (2005), arXiv:0410362 [cond-mat].

M. E. Casida and M. Huix-Rotllant, Annu. Rev. Phys. Chem. 63, 287 (2012), arXiv:1108.0611.

M. A. Marques and E. K. Gross, Annu. Rev. Phys. Chem. 55, 427 (2004).

A. D. Laurent and D. Jacquemin, Int. J. Quantum Chem. 113, 2019 (2013).

E. R. Kjellgren, E. D. Hedegård, and H. J. A. Jensen, J. Chem. Phys. 151, 10.1063/1.5119312 (2019).

V. P. Oisinga, S. J. Van Gisbergen, J. G. Snijders, and E. J. Baerends, J. Chem. Phys. 106, 5091 (1997).

F. Aiga, T. Tada, and R. Yoshimura, J. Chem. Phys. 111, 2878 (1999).
A. Castro, M. A. Marques, J. A. Alonso, G. F. Bertsch, and A. Rubio, Eur. Phys. J. D 28, 211 (2004), arXiv:0206307 [cond-mat].

E. D. Hedegård, F. Heiden, S. Knecht, E. Fromager, and H. J. A. Jensen, J. Chem. Phys. 139, 1 (2013).

E. Fromager, S. Knecht, and H. J. A. Jensen, J. Chem. Phys. 138, 10.1063/1.4792199 (2013), arXiv:1211.4829.

P. Salek, O. Vahtras, T. Helgaker, and H. Ågren, J. Chem. Phys. 117, 9630 (2002).

I. Tunell, Z. Rinkevicius, O. Vahtras, P. Salek, T. Helgaker, and H. Agren, J. Chem. Phys. 119, 11024 (2003).

O. Christiansen, P. Jørgensen, and C. Hättig, International Journal of Quantum Chemistry 68, 1 (1998).

D. A. Telnov and S. I. Chu, Chemical Physics Letters 264, 466 (1997).

P. Salek, T. Helgaker, and T. Saue, Chemical Physics 311, 187 (2005).

B. M. Deb and S. K. Ghosh, The Journal of Chemical Physics 77, 342 (1982).

N. T. Maitra and K. Burke, Chem. Phys. Lett. 359, 237 (2002).

P. Samal and M. K. Harbola, Chem. Phys. Lett. 433, 204 (2006), arXiv:0611428 [cond-mat].

N. T. Maitra and K. Burke, Chem. Phys. Lett. 441, 167 (2007), arXiv:0704.2084.

V. Kapoor, M. Ruggenthaler, and D. Bauer, Phys. Rev. A - At. Mol. Opt. Phys. 87, 1 (2013).

P. W. Langhoff, S. T. Epstein, and M. Karplus, Reviews of Modern Physics 44, 602 (1972).

A. Mayer, P. Lambin, and P.-O. Åstrand, Nanotechnology 19, 025203 (2008).

H. S. Smalø, P.-O. Åstrand, and A. Mayer, Mol. Phys. 111, 1470 (2013).

S. Haghdani, N. Davari, R. Sandnes, and P.-O. Åstrand, J. Phys. Chem. A 118, 11282 (2014).

J. Hermann and A. Tkatchenko, Phys. Rev. Lett. 124, 146401 (2020).

A. Ambrosetti, A. M. Reilly, R. A. Distasio, and A. Tkatchenko, J. Chem. Phys. 140, 10.1063/1.4865104 (2014).

A. Wildman, G. Donati, F. Lipparini, B. Mennucci, and X. Li, J. Chem. Theory Comput. 15, 43 (2019).

A. J. Misquitta and A. J. Stone, Theor. Chem. Acc. 137, 153 (2018).

J. B. Schriber, D. R. Nascimento, A. Koutsoukas, S. A. Spronk, D. L. Cheney, and C. D. Sherrill, J. Chem. Phys. 154, 184110 (2021).

A. Tkatchenko and M. Scheffler, Phys. Rev. Lett. 102, 73005 (2009).
88J. Toulouse, E. Rebolini, T. Gould, J. F. Dobson, P. Seal, and J. G. Ángyán, J. Chem. Phys. 138, 10.1063/1.4804981 (2013).
89J. E. Rice and N. C. Handy, The Journal of Chemical Physics 94, 4959 (1991).
90A. Stone, Molecular Physics 56, 1065 (1985), https://doi.org/10.1080/0026897850102901.
91J. G. Ángyán, G. Jansen, M. Loss, C. Hättig, and B. A. Heß, Chemical Physics Letters 219, 267 (1994).
92R. M. Martin, Electronic structure: basic theory and practical methods (Cambridge university press, 2020).
93E. Zaremba and W. Kohn, Phys. Rev. B 13, 2270 (1976), arXiv:arXiv:1011.1669v3.
94T. Verstraelen, S. Vandenbrande, F. Heidar-Zadeh, L. Vanduyfhuys, V. Van Speybroeck, M. Waroquier, and P. W. Ayers, J. Chem. Theory Comput. 12, 3894 (2016).
95A. D. Becke, J. Chem. Phys. 88, 2547 (1988).
96A. D. Becke and R. M. Dickson, J. Chem. Phys. 89, 2993 (1988).
97M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparrini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian®16 Revision C.01 (2016), gaussian Inc. Wallingford CT.
98T. Verstraelen, P. Tecmer, F. Heidar-Zadeh, C. E. González-Espinoza, M. Chan, T. D. Kim, K. Boguslawski, S. Fias, S. Vandenbrande, D. Berrocal, and P. W. Ayers, Horton 2.1.1 (2017).
99V. I. Lebedev and D. Laikov, Doklady Mathematics 59, 477 (1999).
100P. Hohenberg and W. Kohn, Phys. Rev. 136, B864 (1964).
101W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
102J. C. Slater, The self-Consistent Field for Molecular and solids 4 (1974).
103S. H. Vosko, L. Wilk, and M. Nusair, Can. J. Phys. 58, 1200 (1980).
K. Aidas, C. Angeli, K. L. Bak, V. Bakken, R. Bast, L. Boman, O. Christiansen, R. Cimiraglia, S. Coriani, P. Dahle, E. K. Dalskøv, U. Ekström, T. Enevoldsen, J. J. Eriksen, P. Ettenhuber, B. Fernández, L. Ferrighi, H. Fliegl, L. Frediani, K. Hald, A. Halkier, C. Hättig, H. Heiberg, T. Helgaker, A. C. Hennum, H. Hettema, E. Hjertenæs, S. Høst, I. M. Høyvik, M. F. Iozzi, B. Jansík, H. J. A. Jensen, D. Jonsson, P. Jørgensen, J. Kauczor, S. Kirpekar, T. Kjærgaard, W. Klopper, S. Knecht, R. Kobayashi, H. Koch, J. Kongsted, A. Krapp, K. Kristensen, A. Ligabue, O. B. Lutnæs, J. I. Melo, K. V. Mikkelsen, R. H. Myhre, C. Neiss, C. B. Nielsen, P. Norman, J. Olsen, J. M. H. Olsen, A. Osted, M. J. Packer, F. Pawlowski, T. B. Pedersen, P. F. Provasi, S. Reine, Z. Rinkevicius, T. A. Ruden, K. Ruud, V. V. Rybkin, P. Salek, C. C. Samson, A. S. de Merás, T. Saue, S. P. Sauer, B. Schimmelpfennig, K. Sneskov, A. H. Steindal, K. O. Sylvester-Hvid, P. R. Taylor, A. M. Teale, E. I. Tellgren, D. P. Tew, A. J. Thorvaldsen, L. Thøgersen, O. Vahtras, M. A. Watson, D. J. Wilson, M. Ziolkowski, and H. Ågren, Wiley Interdisciplinary Reviews: Computational Molecular Science 4, 269 (2014).

P. Jørgensen, H. J. A. Jensen, and J. Olsen, J. Chem. Phys. 89, 3654 (1988).

J. Olsen, D. L. Yeager, and P. Jørgensen, J. Chem. Phys. 91, 381 (1989).

A. C. Limaye and S. R. Gadre, J. Chem. Phys. 100, 1303 (1994).

K. C. Tang and C. Edmiston, J. Chem. Phys. 52, 997 (1970).

C. Bender, J. Comput. Phys. 9, 547 (1972).

C. D. Sherrill, Notes 12, 1 (2010).

M. E. Casida, in Recent Advances in Density Functional Methods, edited by D. P. Chong (World Scientific, 1995) pp. 155–192.
Supplementary Material for “A new framework for frequency-dependent polarizable force fields”

YingXing Cheng and Toon Verstraelen

Center for Molecular Modeling (CMM), Ghent University - Technologiepark-Zwijnaarde 46, B-9052 Gent, Belgium

(*Electronic mail: toon.verstraelen@ugent.be)

(Dated: 7 September 2022)
I. ADDITIONAL DISPLAY ITEMS

FIG. S1. Comparison of spectra calculated by ACKS2ω@PBE and LrTDPBE methods for C$_3$H$_6$, C$_3$H$_7$OH, C$_3$H$_8$, C$_4$H$_{10}$, C$_4$H$_{10}$O, C$_4$H$_8$, C$_5$H$_{12}$, C$_6$H$_{14}$, and C$_6$H$_6$.

REFERENCES
FIG. S2. Comparison of spectra calculated by ACKS2ω@PBE and LrTDPBE methods for C$_7$H$_{16}$, C$_8$H$_{18}$, CCl$_4$, CH$_3$CH$_2$OCH$_2$CH$_3$, CH$_3$CH$_3$CH$_3$N, CH$_3$CHO, CH$_3$COCH$_3$, CH$_3$NH$_2$, and CH$_3$NHCH$_3$. 
FIG. S3. Comparison of spectra calculated by ACKS2ω@PBE and LrTDPBE methods for CH₃OCH₃, CH₃OH, CH₄, Cl₂, CO₂, CO, COS, CS₂, and H₂CO.
FIG. S4. Comparison of spectra calculated by ACKS2ω@PBE and LrTDPBE methods for H$_2$, H$_2$O, H$_2$S, HBr, HCl, HF, N$_2$, N$_2$O, and NH$_3$. 

5
FIG. S5. Comparison of spectra calculated by ACKS2ω@PBE and LrTDPBE methods for SiH$_4$ and SO$_2$. 