Letter

Optimized Quantum Drude Oscillators for Atomic and Molecular Response Properties

Szabolcs Góger, Almaz Khabibrakhmanov, Ornella Vaccarelli, Dmitry V. Fedorov, and Alexandre Tkatchenko*

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ABSTRACT: The quantum Drude oscillator (QDO) is an efficient yet accurate coarse-grained approach that has been widely used to model electronic and optical response properties of atoms and molecules as well as polarization and dispersion interactions between them. Three effective parameters (frequency, mass, and charge) fully characterize the QDO Hamiltonian and are adjusted to reproduce response properties. However, the soaring success of *coupled* QDOs for many-atom systems remains fundamentally unexplained, and the optimal mapping between atoms/molecules and oscillators has not been established. Here we present an optimized parametrization (OQDO) where the parameters are fixed by using only dipolar properties. For the periodic table of elements as well as small molecules, our model accurately reproduces atomic (spatial) polarization potentials and multipolar dispersion coefficients, elucidating the high promise of the presented model in the development of next-generation quantum-mechanical force fields for (bio)molecular simulations.

Optimized QDO

$\alpha_1 \quad C_6$

$2R_{vdW} \propto \alpha_1^{1/7}$

$\alpha_\ell \quad C_{2n} \quad V_{pol} \cdots$
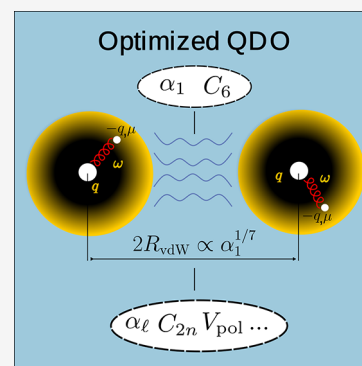
The development of predictive model Hamiltonians that can describe various properties of realistic molecules and materials is a cornerstone of modern physics[1] and chemistry.[2] The quantum Drude oscillator (QDO) is arguably the most powerful Hamiltonian (see the Supporting Information) for accurate and efficient modeling of atomic and molecular response.[1,3–10] Within the coarse-grained QDO model, the response of valence electrons is described *via* a quasi-particle *drudon* with a negative charge $-q$ and mass μ, harmonically bound to a positively charged pseudonucleus of charge q with a characteristic frequency ω. The many-body extension of the QDO model (the *coupled* QDO model) has been widely employed to study both molecules and materials, including their electronic[11,12] and optical[13] properties, polarization,[14,15] dispersion,[7,14,16–24] and exchange[25–27] interactions, as well as a wealth of nonadditive field effects in quantum mechanics[23,28] and quantum electrodynamics.[24,29] Coupled QDOs are also extensively used in the development of van der Waals (vdW) density functionals,[18,30,31] quantum mechanical[1,6] and polarizable force fields,[32–36] as well as recent machine learning force fields.[37,38] Despite such a wide applicability of the coupled QDO model, its success in describing real atoms remains fundamentally unexplained, and the optimal mapping between atoms and oscillators has not been established. In this Letter, we develop an optimized parametrization (OQDO) in which the parameters are fixed by using only the well-known atomic dipolar properties. Remarkably, the OQDO reproduces spatial atomic polarization potentials and atomic multipolar dispersion coefficients. Our OQDO model for atoms and small molecules also paves the way to the development of next-

generation quantum-mechanical force fields for (bio)molecular simulations.

The three parameters $\{q, \mu, \omega\}$ fully define the QDO, and three atomic response properties could be chosen to fix them, meaning that the choice of QDO parameters is not unique. In addition, all QDO response properties, multipolar polarizabilities and dispersion coefficients, are uniquely fixed by the three parameters *via* closed-form relations.[6] The static dipole polarizability of a QDO, $\alpha_1 = q^2/\mu\omega^2$, conveniently combines all three parameters, and it is natural to set this expression to the reference atomic α_1. The QDO expression for the dipole−dipole dispersion coefficient $C_6 = \frac{3}{4}\hbar\omega\alpha_1^2$ is identical to the London formula and allows to fix ω if the reference atomic values of C_6 and α_1 are given. Since α_1 and C_6 are accurately known for all elements in the periodic table,[39–41] they form a baseline for the QDO parametrization. However, one more condition is required to obtain $\{q, \mu, \omega\}$, for which different constraints can be imposed. A reasonable idea is to fix $q = 1$ au since a QDO should reproduce the response of electrons. This results in the fixed-charge QDO (FQDO):
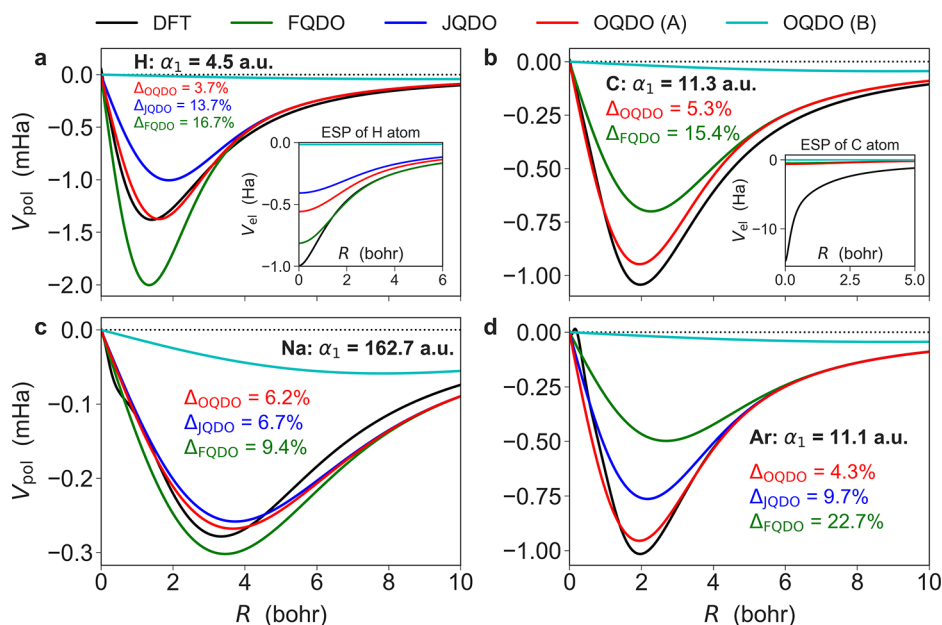
Figure 1. Polarization potential curves $V_{\text{pol}}(\mathbf{r})$ calculated with DFT-PBE0 and various QDO parametrizations for (a) hydrogen, (b) carbon (no JQDO values are available), (c) sodium, and (d) argon atoms. The FQDO and JQDO parametrization schemes are described in eqs 1 and 2, respectively. OQDO(A) and OQDO(B) correspond to the two solutions of the transcendental equation given by eq 3. In all cases, the direction along the applied field was chosen for the plots. The reference values for dipole polarizability α_1 are shown for each element. The numerical values of the normalized root−mean−square error (Δ) are displayed for the three QDO flavors. For hydrogen and carbon atoms, the unperturbed electrostatic potentials (ESP) $V_{\text{el}}(\mathbf{r})$ are shown as insets, indicating that a QDO captures the response of atomic electron density but not the static potential itself.

$$q = 1, \quad \omega = 4C_6/3\hbar\alpha_1^2, \quad \mu = 9\hbar^2\alpha_1^3/16C_6^2 \qquad (1)$$

However, fixing q and using QDO recursion relations for high-order response usually yields large errors in the multipolar response properties (see Figure 3 and refs 42 and 43). A more rigorous approach was suggested by Jones et al.[6] by employing the dipole−quadrupole dispersion coefficient C_8. The mapping $\{\alpha_1, C_6, C_8\} \rightarrow \{q, \mu, \omega\}$ yields the Jones QDO (JQDO) parametrization scheme:

$$q = \sqrt{\mu\omega^2\alpha_1}, \quad \omega = 4C_6/3\hbar\alpha_1^2, \quad \mu = 5\hbar C_6/\omega C_8 \qquad (2)$$

The JQDO approach improves the multipolar response over the FQDO model, while simulations using the coupled JQDO model captured many remarkable properties of bulk water and its surface.[35,44] However, the C_8 dispersion coefficient is not directly measurable, and accurate *ab initio* calculations of quadrupole (α_2) and octupole (α_3) polarizabilities and $C_8−C_{10}$ dispersion coefficients are currently technically feasible only for closed-shell species (noble-gas atoms and small molecules) or alkali and alkaline-earth atoms with s valence shells.[45−48] For other open-shell atoms (containing p, d, or f valence shells), convergence of quantum-chemical response calculations becomes a technical hurdle[49] (see also additional discussion in the Supporting Information). Thus, using higher-order atomic response properties does not lead to a parametrization that would be universally applicable across the periodic table as well as for small molecules.

Here, we introduce an optimized QDO parametrization (OQDO), where we effectively map dipolar atomic quantities $\{\alpha_1, C_6\}$ to the oscillator parameters. The third parameter is fixed by using the force balance equation for vdW-bonded dimers derived recently.[25−27] Two equations for q and ω follow the JQDO scheme, whereas the third one is replaced

with a transcendental equation for a product $\mu\omega$ to be solved numerically (*vide infra*)

$$\mu = \frac{5\hbar C_6}{\omega C_8} \rightarrow \exp\left(\frac{2\mu\omega R_{\text{vdW}}^2}{\hbar}\right) = \frac{2^7 \times (\alpha_{\text{fsc}}^{-1/3}a_0)^4}{(3\hbar/\mu\omega)^2} \qquad (3)$$

where $\alpha_{\text{fsc}} = e^2/4\pi\varepsilon_0\hbar c$ is the fine-structure constant and a_0 is Bohr's radius. The vdW radius (R_{vdW}) is calculated *via* the universal formula connecting it with the dipole polarizability

$$\alpha_1(R_{\text{vdW}}) = (4\pi\varepsilon_0)R_{\text{vdW}}^7/(\alpha_{\text{fsc}}^{-1/3}a_0)^4 \qquad (4)$$

as established in ref 27 for atoms in the periodic table. Comparing it with its counterpart

$$\alpha_1(\mu\omega, R_{\text{vdW}}) = (4\pi\varepsilon_0)R_{\text{vdW}}^7 \frac{2^7(\mu\omega/3\hbar)^2}{\exp(2\mu\omega R_{\text{vdW}}^2/\hbar)} \qquad (5)$$

which was obtained within the QDO model,[25,26] delivers eq 3 to determine μ from $\mu\omega$.

The QDO Hamiltonian effectively captures the integrated atomic response. However, when modeling molecules or solids, coupled QDOs must properly describe noncovalent interactions between atoms. Considering two fragments i and j and using interatomic perturbation theory,[50,51] the interaction energy can be written as the integrated product of the electron density of moiety i with the electric potential generated by moiety j:[50,52]

$$E_{\text{int}} = \int \rho_i(\mathbf{r})V_j(\mathbf{r})d^3\mathbf{r} \qquad (6)$$

This formula is valid for all noncovalent interactions: electrostatics, induction, exchange-repulsion, and dispersion. Its validity is evident for the former two cases,[50,52] and it was shown that exchange[53] and dispersion[54−56] interactions can be
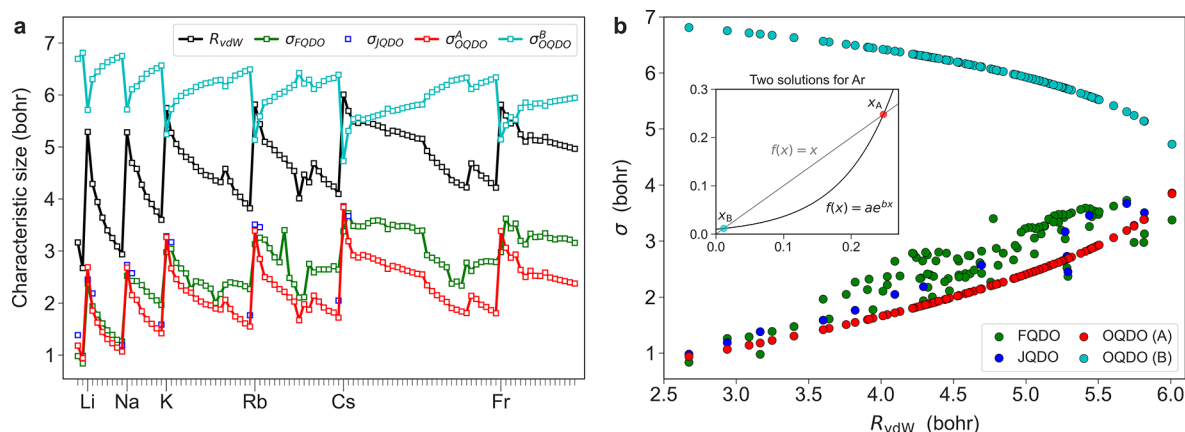
Figure 2. (a) Periodic variations of the QDO length $\sigma = \sqrt{\hbar/2\mu\omega}$ with the atomic number for the three different parametrizations, as compared to the atomic vdW radii (R_{vdW}), which are evaluated *via* eq 4 using the reference atomic polarizabilities.[39] (b) Correlation between R_{vdW} and σ (within the three QDO parametrizations) for 102 elements in the periodic table. The schemes of OQDO(A) and OQDO(B) correspond to two solutions of eq 11, as illustrated using the example of Ar in the inset.

represented using the form of eq 6 with ρ and V being *effective* quantities different from free-atom counterparts. The argument that dispersion interactions can be written using eq 6 goes back to Feynman's consideration of molecular forces,[54] which was further elaborated by Hunt[55] with a focus on dispersion forces and finally extended to dispersion energies with a demonstration of its validity for real molecules and materials.[57,58]

Response properties are given by variations of E_{int} as

$$\delta E_{int} = \int (\delta\rho_i(\mathbf{r})V_j(\mathbf{r}) + \rho_i(\mathbf{r})\delta V_j(\mathbf{r}))d^3\mathbf{r} \quad (7)$$

For an external electric field $\mathbf{E}$, which can also model the effect of environment, $\delta\rho(\mathbf{r}) = \rho_E(\mathbf{r}) - \rho(\mathbf{r})$, where $\rho_E(\mathbf{r})$ is the electron density under the external field. Then the dominant contribution to $\delta V_j(\mathbf{r})$ is generated by the corresponding $\delta\rho_j(\mathbf{r}')$ via the polarization potential[59]

$$V_{pol}(\mathbf{r}) = -\frac{1}{4\pi\varepsilon_0} \int \frac{\rho_E(\mathbf{r}') - \rho(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d^3\mathbf{r}' \quad (8)$$

which describes the change in the electrostatic potential of the system due to the polarization of its charge density by the presence of another moiety (an electric field in this case). For the QDO in a uniform electric field, the integral in eq 8 can be evaluated analytically as

$$V_{pol}^{QDO}(\mathbf{r}) = \frac{-q}{4\pi\varepsilon_0}\left(\frac{\mathrm{erf}(\tilde{r}/\sigma\sqrt{2})}{\tilde{r}} - \frac{\mathrm{erf}(r/\sigma\sqrt{2})}{r}\right) \quad (9)$$

where $\tilde{r} = \mathbf{r} - \alpha_1\mathbf{E}/q$ is the field-induced oscillator coordinate and $\sigma = \sqrt{\hbar/2\mu\omega}$ is the QDO spread.[60] In the Supporting Information, we present $V_{pol}^{QDO}(\mathbf{r})$ in comparison to $V_{pol}(\mathbf{r})$ calculated for 21 atoms (between H–Ca and Kr) within hybrid density functional theory DFT-PBE0[61−65] shown to yield a highly accurate description of electronic response[66] comparable to coupled-cluster calculations (see the Supporting Information). Here, we remark that the strength of the electric field was chosen individually for each element depending on its reference static dipole polarizability[39,41] so that the field-induced dipole moment is set as $\mathbf{d} = \alpha_1\mathbf{E} = 0.01$ au for all atoms.[67]

Before comparing $V_{pol}(\mathbf{r})$ for real atoms with different QDO flavors, it is instructive to consider which atomic properties can

be faithfully captured by a QDO. First, the QDO does not aim to describe static properties of the atomic electron density but rather its response under applied static and fluctuating fields, as demonstrated also by the insets in Figure 1a,b. The electrostatic potential (ESP) of a QDO is given by $V_{el}^{QDO} = -q\mathrm{erf}(r/\sigma\sqrt{2})/r$, so the charge q determines its magnitude. This explains why V_{el}^{FQDO} yields good agreement with V_{el}^{DFT} for hydrogen. However, the QDO model does not describe V_{el} for many-electron atoms because $q \approx 1$ au, while the ESP of atoms scales nonlinearly with Z (see the example of carbon in the inset of Figure 1b). Second, the harmonic response captured by a QDO model should be sufficient to accurately describe integrated electronic displacements induced by weak fields. However, it is much less clear how well different QDO parametrizations perform for distributed polarization potentials described by eq 8 for many-electron systems, given the analytical form of $V_{pol}^{QDO}(\mathbf{r})$ in eq 9. To answer this question, in Figure 1 we compare the V_{pol} curves of real atoms and $V_{pol}^{QDO}(\mathbf{r})$ employing the three QDO models discussed above. We used the accurate *ab initio* reference data on α_1 and C_6[39,41,68] to parametrize FQDO and OQDO. When available, we also used the analogous data on C_8[45−47] to parametrize the JQDO model. We observe that the OQDO model is able to reproduce the full range of the polarization potential of real atoms with a reasonable accuracy, showing significantly better agreement with the DFT-PBE0 results than FQDO and JQDO. To quantify this, for each atom, we calculated the root−mean−squared-error (RMSE) of the three QDO curves with respect to the PBE0 reference curves and normalized the RMSE using the equilibrium depth of the PBE0 curve. The OQDO flavor has an error of 8.9% when averaged over 21 atoms, whereas JQDO and FQDO yield average errors of 13.2% and 15.4%, respectively. We also emphasize that the predictions of the OQDO model remain accurate for many-electron atoms such as noble gases and alkali metals. It is especially reassuring that the OQDO model reproduces the nonlinear $V_{pol}(\mathbf{r})$ curves obtained from DFT calculations without any adjustments. In fact, the performance of the OQDO is sensitive to variations in the QDO parameters (solutions A or B in Figure 1), so the satisfactory agreement shows that the chosen OQDO(A) model accurately describes real atoms. The significant differences between the predictions
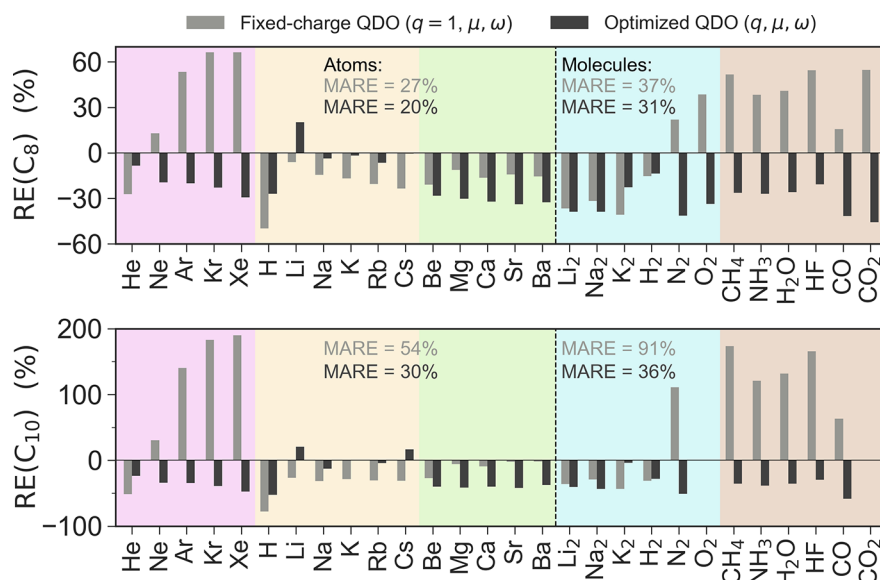
Figure 3. Multipolar dispersion coefficients C_8 and C_{10} as predicted by the FQDO ($q = 1$) and OQDO models. Relative error RE = $(C_j - C_j^{\text{ref}})/C_j^{\text{ref}}$ with respect to *ab initio* reference data[45−48] is plotted. For the two models, numerical values of mean absolute relative errors (MARE) are evaluated separately for atoms and molecules. In the cases of O_2 and CO_2, no reliable *ab initio* reference data for C_{10} could be found.

of various parametrizations for $V_{\text{pol}}(\mathbf{r})$ underline the importance of optimal mapping between atomic response properties and QDO parameters.

We discuss now the technical aspects of deriving the two solutions of the OQDO model (labeled as OQDO(A) and OQDO(B) in Figure 1 and the Supporting Information) and their connection to real atoms. The starting point is eq 4 that connects the atomic vdW radius and its dipole polarizability. Within the QDO model, eq 4 can be written as follows:[26]

$$\alpha_1(\mu\omega,\ R_{\text{vdW}}) = \frac{2^7(4\pi\varepsilon_0)R_{\text{vdW}}^7}{(3\hbar/\mu\omega)^2\exp(2\mu\omega R_{\text{vdW}}^2/\hbar)} \tag{10}$$

The OQDO parametrization imposes that the product $\mu\omega$ in eq 10 delivers the same R_{vdW} as from eq 4, for $\alpha_1(\mu\omega, R_{\text{vdW}}) = \alpha_1(R_{\text{vdW}})$. For simplicity, we rewrite eq 10 in terms of the dimensionless variable x as

$$x = ae^{bx}, \quad x = \mu\omega a_0^2/\hbar = a_0^2/2\sigma^2 \tag{11}$$

with the dimensionless coefficients a and b given by

$$a = \frac{3\alpha_{\text{fsc}}^{2/3}}{8\sqrt{2}}, \quad b = \frac{R_{\text{vdW}}^2}{a_0^2} = \frac{(\alpha_1/4\pi\varepsilon_0)^{2/7}}{\alpha_{\text{fsc}}^{8/21}a_0^{6/7}} \tag{12}$$

where we used eq 4 to express R_{vdW} in terms of α_1. For all elements in the periodic table, we found that eq 11 has two solutions, A and B. This is illustrated by the inset of Figure 2b for the case of Ar. It is instructive to consider that eq 11 has one solution when the polarizability of an atom is equal to the critical value:

$$\alpha_1^{(c)}/4\pi\varepsilon_0 = (8\sqrt{2}/3e)^{7/2}\alpha_{\text{fsc}}^{-1}a_0^3 \approx 431 \text{ au} \tag{13}$$

which is greater than the largest atomic dipole polarizability ($\alpha_1 \approx 400$ au) of Cs.[41] The existence of two solutions extends beyond the employed QDO model. We obtained an analogous result by using the Tang-Toennies potential[69] with the repulsive interaction treated by the Born-Mayer form (see the Supporting Information).

Since the frequency of the OQDO is fixed by the second condition of eqs 1 and 2, solutions A and B for the product $\mu\omega$ differ both in mass and charge, yielding quite different results. First, $V_{\text{pol}}^{\text{QDO}}(\mathbf{r})$ constructed from solution B does not resemble DFT potentials, while A is in good agreement with them (Figure 1). Second, the overlap integral $S = \exp\left(-\frac{\mu\omega}{2\hbar}R_{\text{eq}}^2\right)$ between two QDOs at their equilibrium distance $R_{\text{eq}} = 2R_{\text{vdW}}$ is significantly larger for solution B, which violates the initial assumption used to derive eq 10 that S is small at R_{eq}.[26] Third, the QDO length σ constructed from solution A follows the same periodic trend as the atomic vdW radii, whereas solution B does not seem to correlate well (Figure 2a). Therefore, throughout this work we refer to solution A as the optimized parametrization. For 102 atoms, the full set of QDO parameters corresponding to both solutions A and B is presented in the Supporting Information together with the reference values of $\{\alpha_1, C_6\}$. Another noteworthy property of the OQDO model (see Figure 2b) is a clear correlation between the QDO length (model quantity) and the atomic vdW radius (physical observable). In fact, these quantities should be connected *via* the dipole polarizability.[26,60] This property is not captured well by either the FQDO or the JQDO models.

For practical calculations of the vdW energy and constructing predictive force fields, the multipolar contributions associated with the C_8 and C_{10} coefficients can become relevant.[42,43,48] The available reference data for higher-order molecular dispersion coefficients have significant uncertainties. Our careful examination of the literature reporting the reference values of C_8 and C_{10} (see refs 45−48. and references therein) identifies uncertainties of up to 20% for the reference C_8 and C_{10} values. Within the QDO formalism, it is straightforward to evaluate these coefficients using closed-form expressions derived by Jones et al.[6] In Figure 3, we present the predictions of C_8 and C_{10} by FQDO and OQDO models as compared to accurate reference values compiled from the literature[45−48] for a set of 16 atoms (including alkali and alkaline-earth metals and noble gases) and 12 small

molecules. Overall, our results show that the OQDO parametrization improves the dispersion coefficients compared to the FQDO one, reducing the MARE from 31% to 25% for C_8 and from 68% to 33% for C_{10} when averaged over all 28 (26 for C_{10}) systems. The OQDO model consistently surpasses the FQDO in accuracy for all systems except for alkaline-earth metals where the FQDO gives more accurate results. Moreover, Figure 3 shows that the deviations of OQDO dispersion coefficients from the reference values are consistent in terms of their sign and magnitude. Namely, for the majority of systems, FQDO underestimates C_8 and C_{10}, but roughly for one-third of them, the dispersion coefficients are over-estimated. The maximal errors of FQDO are observed for Xe in the case of both C_8 (66%) and C_{10} (190%). In contrast, the OQDO consistently underestimates both dispersion coefficients for all systems, except for C_8 of Li as well as C_{10} of Li and Cs. The maximum errors of the OQDO are observed for CO_2 (46%) in the case of C_8 and CO (58%) in the case of C_{10}, which are significantly smaller than maximum errors of the FQDO. The consistency of the OQDO errors allows a straightforward rescaling of dispersion coefficients: with our best rescaling factors, 1.3 for C_8 and 1.5 for C_{10}, one can decrease the MARE of the OQDO to 15% and 22%, respectively, which is commensurate with the uncertainty of the reference molecular C_8 and C_{10} values. A more detailed analysis of the dispersion coefficients (including JQDO and OQDO models as well as their scaled versions) can be found in the Supporting Information, where we also discuss static polarizabilities α_2 and α_3. The latter becomes less important in the QDO approach where the dispersion coefficients, determining the dispersion energy, are directly expressed in terms of QDO parameters. It is important to mention that the effects of three-body interactions are captured by the OQDO scheme on an equal footing with the JQDO scheme. The accuracy in determination of C_6 and C_9 coefficients is known to be comparable.[70] In ref 6, it was shown that within the QDO model the leading three-body dispersion coefficient is given by $C_9 = \alpha_1 C_6/4$. Thus, with the same reference α_1 and C_6, there is no difference between the JQDO and the OQDO para-metrizations.

We presented the OQDO model based on robust para-metrization that solely employs dipolar α_1 and C_6, accurately known for all atoms in the periodic table. The new parametrization scheme dispenses the need for reference higher-order dispersion coefficients and delivers accurate polarization potentials, thereby improving the description of noncovalent interactions at short distances keeping the accuracy of the JQDO model for large distances due to the proper dipolar response. The key point of the proposed parametrization is employing the relation between the dipole polarizability and the vdW radius, both being integrated quantities with many-electron effects included. Thus, the OQDO scheme serves as an optimized and efficient mapping between atoms/molecules and oscillators, which substantially advances our ability to model a wide range of response properties of molecules and materials, also paving the way to develop next-generation quantum-mechanical force fields for (bio)molecular simulations.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpclett.3c01221.

Polarization potentials for 21 chemical elements, OQDO parameters, dispersion coefficients and multipole polar-izabilities, more detailed discussions and computational details (PDF)

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Notes

The authors declare no competing financial interest.

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