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Quantum Mechanics of Drude Oscillators with Full Coulomb Interaction

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Drude oscillators provide a harmonic description of charge fluctuations, and are widely studied as a model system and for *ab initio* calculations. In the dipole approximation the Hamiltonian describing the interaction of Drudes is quadratic, so can be diagonalized exactly, but the energy diverges at short range. Here we consider the quantum mechanics of Drude oscillators interacting through the full Coulombic Hamiltonian, for which the interaction energy does not have this defect. This prototypical model for interactions between matter includes electrostatics, induction and dispersion. Potential energy curves for rare-gas dimers are very closely matched by Drude correlation energies plus a single exponential function. The exact and accurate results presented here help to delineate between basic properties of the physical model, and effects that arise from the dipole approximation.

I. INTRODUCTION

The quantum Drude oscillator¹ provides a minimal model of electrical response properties of matter, and consists of a oppositely charged particles connected by a spring. Drude oscillators have risen to prominence through the development of polarizable force-fields²⁻⁷, as the basis of the Tkatchenko-Scheffler dispersion functional⁸⁻¹³, and in models that describe attachment of electrons to neutral matter¹⁴⁻¹⁷. Their application to the interaction between nanoscale systems with varying dimensionality has revealed collective effects that qualitatively determine the interaction, and that are completely omitted in simpler, pairwise dispersion models¹⁸. One study¹⁹ has gone beyond the dipole limit using both norm-conserving diffusion Monte Carlo and diagrammatic techniques. However, due to use of the multipole expansion, the latter also requires a short-range screening function.

The interaction between well-separated Drude oscillators is often modelled in the dipole approximation, and in this case the Hamiltonian is quadratic in the positions and momenta of the Drude particles, and is diagonalized by a normal-mode transformation^{1,20,21}. Perturbation theory leads to the well known long-range $-C_6/R^6$ form²², and the divergence at short-range is typically removed through a damping correction^{10,23-27}. Use of such damping function, however, introduces a few more parameters in the theory.

Here we study the properties of the basic quantum mechanical model the Drude-oscillator dimer with full Coulombic interaction. As a result, the interaction energies become finite for all inter-Drude distances nullifying the need of any damping function. The results presented here, therefore, can be treated as references to judge the merit of any future approximations. By providing accurate benchmark data we, thus, aim to help validation of more tractable approaches, and to separate effects that are intertwined in damping schemes. We are also interested in this basic system as a prelude to working on embedding schemes that combine electronic and Drude degrees of freedom. Although Drude oscillators

are spherical, and we here apply them to spherical systems, extension to anisotropic systems is straightforward by distribution of Drude-oscillator sites, typically on atomic centres.

II. THEORY

We will consider a three-dimensional Drude oscillator with charges $\pm q$, mass μ and frequency ω , described by a Hamiltonian

$$h = -\frac{\hbar^2}{2\mu}\nabla^2 + \frac{\mu\omega^2}{2}r^2. \quad (1)$$

The quantum states are labelled by the number of quanta in each Cartesian direction $|n_x n_y n_z\rangle \equiv |\mathbf{n}\rangle$, and have energies $\hbar\omega(n + 3/2)$ where $n = n_x + n_y + n_z$.

The system of two Drude oscillators is described by a Hamiltonian $H = H_0 + V$, where $H_0 = h_1 + h_2$ and V is the interaction. In the dipole approximation the interaction is given by

$$V_{\text{dip}} = \frac{q^2}{4\pi\epsilon_0 R^5} \left\{ R^2 \mathbf{r}_1 \cdot \mathbf{r}_2 - 3 (\mathbf{r}_1 \cdot \mathbf{R}) (\mathbf{r}_2 \cdot \mathbf{R}) \right\}, \quad (2)$$

where \mathbf{r}_1 and \mathbf{r}_2 are the Drude coordinates, and \mathbf{R} is the vector connecting the fixed positive charges of the two oscillators. Note that the quadratic form of dipole approximated potential allows an exact solution of the model. However, within this approximation the oscillators always retains its spherical shapes and do not provide any induction interactions. However, a realistic model of molecular electron density needs to be polarizable. The exact interaction is given by

$$V = \frac{q^2}{4\pi\epsilon_0} \left\{ \frac{1}{R} + \frac{1}{|\mathbf{R} - \mathbf{r}_1 + \mathbf{r}_2|} - \frac{1}{|\mathbf{R} - \mathbf{r}_1|} - \frac{1}{|\mathbf{R} + \mathbf{r}_2|} \right\}, \quad (3)$$

where each term describes the Coulombic interaction between charges associated with each oscillator. The first

two repulsive terms mimic internuclear and interelectronic interactions while the last two attractive terms represent electron-nucleus attractions. The presence of both repulsive as well as attractive interactions makes the model progressively polarizable with decreasing separation between them.

With energies expressed in units $\hbar\omega$ and lengths in $\sqrt{\hbar/(\mu\omega)}$, the system is fully defined by the two parameters that specify the relative strength and relative length-scale of the interaction term. For weak interaction (the small q limit) the phenomenology is dominated by the harmonic oscillator portion of the Hamiltonian. For strong interaction (large q) the harmonic constraint is relatively weak, and the system behaves rather like a harmonically coupled pair of hydrogen atoms, with the negative particle of oscillator 1 interacting with the positive particle of oscillator 2, and *vice versa*.

The zeroth-order Hamiltonian is diagonal in the product basis $|\mathbf{n}_1\mathbf{n}_2\rangle$, with elements

$$\langle \mathbf{n}_1\mathbf{n}_2 | H_0 | \mathbf{n}_1\mathbf{n}_2 \rangle = (3 + n_1 + n_2)\hbar\omega, \quad (4)$$

and in particular the zeroth-order energy is $E_0 = 3\hbar\omega$.

The interaction matrix elements over V have the form of electrostatic interactions between Hermite-Gaussian charge distributions and point charges, so the required integrals have exactly the same form as the electron-repulsion integrals and the nuclear-attraction integrals routinely evaluated in molecular quantum chemistry²⁸; we evaluate them following the same methods.

The reference approach is exact diagonalization (or full configuration interaction — FCI) truncated to at most m quanta at either site. We also explore perturbation theory (PT) to arbitrary order²⁹ and the random-phase approximation (RPA)^{30,31}. RPA is of interest because it provides the exact ground state for $H_0 + V_{\text{dip}}$.

III. RESULTS

We perform calculations on pairs of Drude oscillators parameterized to reproduce the dipolar polarizability and C_6 and C_8 dispersion coefficients for helium, neon and argon atoms by Jones *et al.*³² — the parameters can be found in Table I of that work.

A. Mean field effects

The expectation value

$$\langle \mathbf{00} | H | \mathbf{00} \rangle = E_0 + E_1, \quad (5)$$

where $E_1 = \langle \mathbf{00} | V | \mathbf{00} \rangle$, is the simplest type of mean-field energy. In discussing total energies E we use the term “binding energy” to denote $E - E_0$, and “correlation energy” for $E_{\text{corr}} = E - E_0 - E_1$. (In the dipole approximation these quantities are identical.) Using $\zeta = m\omega$,

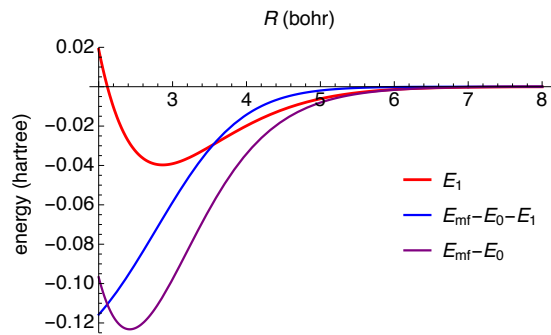


FIG. 1: Mean-field contributions to the interaction of two Drude oscillators, parameterized for argon dimer, with $m = 5$. The curves show E_1 , the purely electrostatic interaction of ground-state oscillators; $E_{\text{mf}} - E_0 - E_1$, the induction contribution to the interaction; and $E_{\text{mf}} - E_0$ the total mean-field binding energy.

the first-order energy is

$$E_1 = \frac{q^2}{4\pi\epsilon_0} \left\{ \frac{1}{R} + \frac{\text{erf}(\sqrt{\zeta}/2R)}{R} - 2 \frac{\text{erf}(\sqrt{\zeta}R)}{R} \right\}. \quad (6)$$

In the dipole approximation, dimer states with an excitation on just one site, such as $|000, 100\rangle$ make no contribution to the ground-state wavefunction. With the full interaction, though, they do contribute, and describe induction effects³³. By diagonalizing the configuration-interaction-singles (CIS) block of the Hamiltonian, we can capture just this induction effect; the CIS ground-state is exactly the same as would result from a self-consistent-field calculation with a mean-field (i.e. product-type) wavefunction, and we label the energy from this calculation E_{mf} .

The mean-field contributions to binding are shown in Figure 1. The interactions are strong, but very short-ranged. Although the key phenomena are captured, the functional form and range is not correct: in the Drude model these follow from the Gaussian charge distribution, which is obviously a very poor model for the electron density of the atom; and moreover, the lengthscale is determined to fit response properties, rather than the size of the atom. These attractive interactions are less relevant in the true argon dimer, where exchange-repulsion effects dominate at such distances.

B. Full configuration interaction

We compute FCI correlation energies with the number of quanta at a single site truncated at m , so the Hilbert space that is diagonalized has dimension d^2 where $d = \binom{m+3}{3}$. As is often observed^{34,35} we find that the FCI correlation energy converges as $1/d$, as illustrated in Figure 2. Extrapolation allows us to estimate the correlation energy of this system to be $-0.902 \text{ m}E_h$. The comparable $m = 1$ calculation yields only $-0.508 \text{ m}E_h$, and in the dipole approximation $-C_6/R^6 = -0.571 \text{ m}E_h$ is

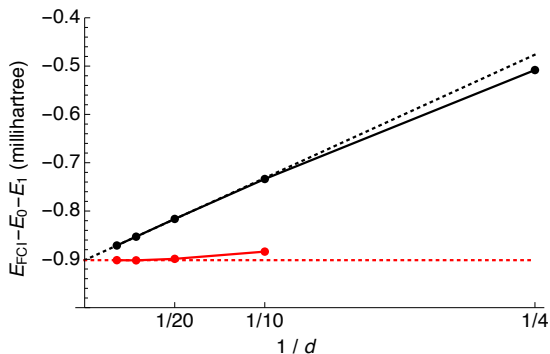


FIG. 2: Convergence of FCI correlation energies as a function of m for argon dimer with internuclear separation $R = 7$ bohr, with (red) and without (black) extrapolation assuming $1/d$ convergence.

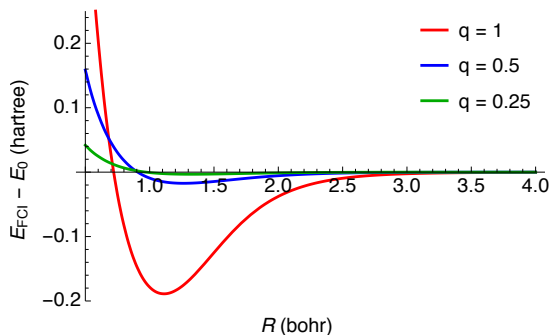


FIG. 3: Variation of binding curves for two Drude oscillators for representative values of q and for $\omega = \mu = 1$, computed using the $1/d$ extrapolation with $m = 4, 5$.

obtained. Around the optimum interatomic separation, $-C_6/R^6$ is *larger* than the interaction energy obtained with the full Hamiltonian and $m = 1$; but it is *smaller* than the full interaction, and this may have implications for the design of damping functions.

As noted above, the system in reduced units is characterized by the parameters q and R , and we show highly accurate results for the binding energy of the dimer as a function of these variables in Figure 3.

C. Perturbation theory and RPA

An obvious approach to the description of this system is perturbation theory. Dispersion appears first at second order (as does induction, discussed above). Although we have efficient implementations of second- and third-order perturbation theory (PT2 and PT3), we here use the FCI program, following the approach of Ref. 29, to investigate the convergence at higher orders. The p th-order wavefunction is computed in terms of lower-order contributions as

$$|\psi_p\rangle = -(H_0 - E_0)^{-1} \sum_{k=1}^p (\delta_{k1} V - E_k) |\psi_{p-k}\rangle \quad (7)$$

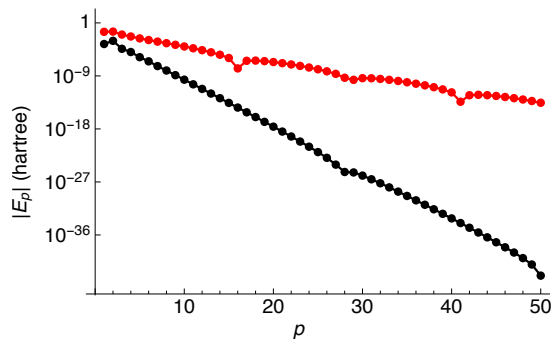


FIG. 4: Convergence of the magnitudes of perturbative energy contributions E_p for argon dimer at two interatomic separations, $R = 7$ bohr (black) and $R = 3.5$ bohr (red), computed with $m = 5$.

with each successive energy given by $E_{p+1} = \langle \psi_0 | V | \psi_p \rangle$.

The convergence of the perturbation series for argon dimer is shown in Figure 4 for two interatomic separations; in both cases convergence is rapid and smooth. The slight surprise here is that the perturbation theory is smoothly convergent even when the atoms are extremely close; this is in contrast to the Møller-Plesset series, which often diverges³⁶⁻³⁸.

RPA supplies the exact ground-state energy in the dipole approximation (because $H_0 + V_{\text{dip}}$ is harmonic), but is approximate for the fully interacting Hamiltonian; here we assess its accuracy. The RPA correlation energy was evaluated using

$$E_{\text{RPA}}^{\text{corr}} = \frac{1}{2} \sum_n (\omega_n^{\text{RPA}} - \omega_n^{\text{CIS}}) \quad (8)$$

where $|\omega_n^{\text{RPA}}|^2$ are the eigenvalues of the RPA matrix $\mathbf{M} = (\mathbf{A} + \mathbf{B})(\mathbf{A} - \mathbf{B})$, where $A_{\mathbf{nn}'} = \langle \mathbf{n}\mathbf{0} | H - E_0 | \mathbf{0}\mathbf{n}' \rangle$ and $B_{\mathbf{nn}'} = \langle \mathbf{0}\mathbf{0} | V | \mathbf{nn}' \rangle$, and where ω_n^{CIS} are the CIS eigenvalues.

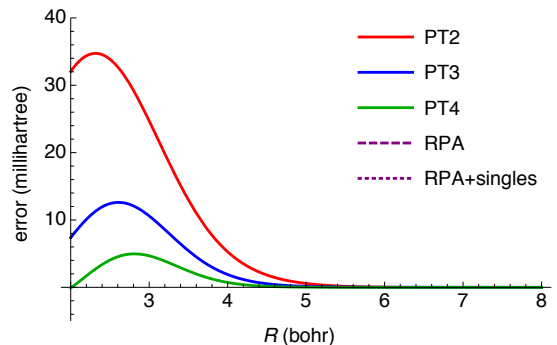


FIG. 5: Errors in leading-order perturbation theory and RPA (relative to FCI) for the argon dimer and with $m = 3$. RPA is shown with and without a singles correction, computed as the CIS induction contribution.

The errors in energies for argon dimer computed using RPA and leading orders of PT are plotted in Figure 5,

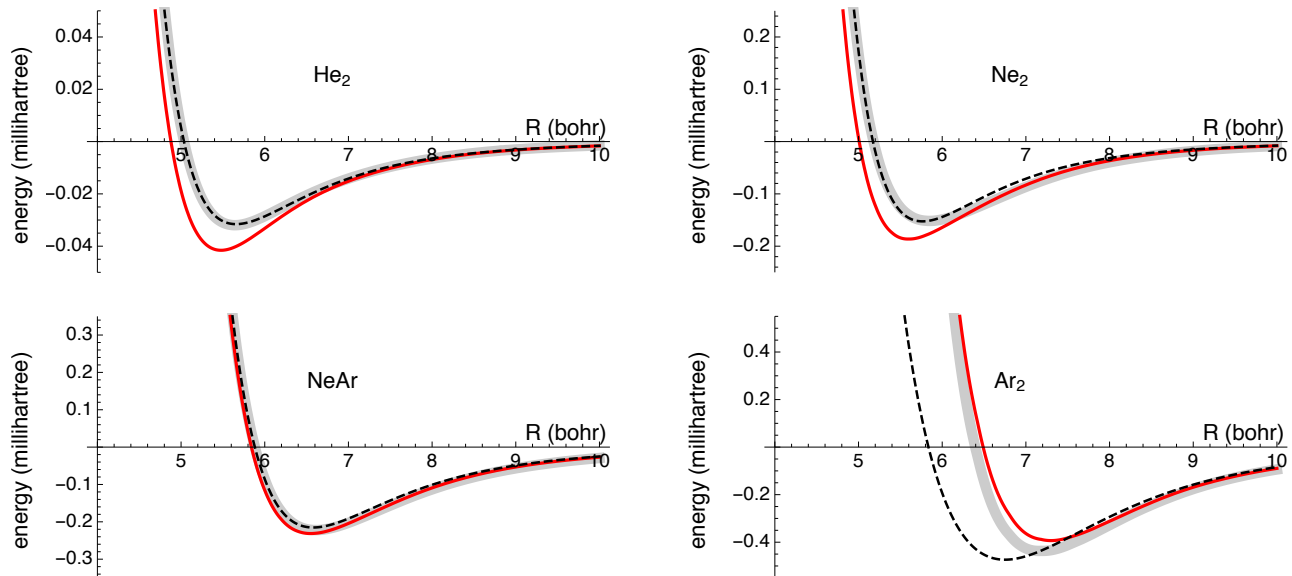


FIG. 6: Comparison of Drude and *ab initio* binding energy curves for He_2 , Ne_2 , NeAr and Ar_2 . The thick gray lines provide the reference *ab initio* CCSD(T) potentials (see text). Red, solid lines are the sum of the *ab initio* HF energy and the Drude correlation energy computed with exact diagonalization and $m = 5$. The dashed lines show the two-parameter fit $ae^{-bR} + E_{\text{corr}}(R)$, providing almost perfect agreement with the *ab initio* binding curves.

computed relative to FCI. Rapid convergence of the perturbation series is confirmed. Clearly RPA performs less well, despite being exact for dipole-interaction Hamiltonian. At short range this is mostly due to omission of single excitations — in the dipole approximation these vanish, but with the full Hamiltonian they do not. They would be properly accounted for by basing the RPA calculation on a relaxed mean-field reference state, rather than on the zeroth-order wavefunction used here. But even the simpler expedient of adding the relaxation terms from CIS clearly improves matters in the short range.

What is more surprising is that the convergence to the correct long-range form is slower for RPA than even for PT2, although it does eventually reach the correct asymptote. Although RPA produces the correct C_6 coefficient, higher-order multipole contributions (C_8 , C_{10} , etc) appear not to be as accurate as in PT n . While this is clearly consistent with the observation that RPA is exact in the dipole approximation, it was surprising to us.

D. Comparison against *ab initio* results

Finally we assess the accuracy of the Drude model of correlation effects in the pairwise interaction of rare-gas atoms. Our reference data are obtained using CCSD(T)/aug-cc-pVQZ³⁹ with counterpoise corrections⁴⁰, an approach that produces rare-gas dimer binding energies sufficiently accurate for our purposes.

Correlation energies were computed using FCI with

$m = 5$. We then investigated two models for the remaining interaction effects: first using *ab initio* Hartree-Fock (HF) theory (with the aug-cc-pVQZ basis set), and second by fitting a single exponential. The results are plotted in Figure 6 for He_2 , Ne_2 , NeAr and Ar_2 . It can be seen that reasonable agreement is found between $E_{\text{HF}} + E_{\text{corr}}$ and the reference data, despite the complete absence of dimer-specific parameters.

A key source of error in these calculations is the failure to treat any fermionic exchange effects beyond the HF level. Broadly such effects are well approximated by an exponential with a length-scale commensurate with the size of the atom; the dominant exchange-repulsion and induction effects of HF theory can be expected to follow a similar form. We therefore fit $ae^{-bR} + E_{\text{corr}}(R)$ with respect to the parameters a , b ; the quality of this fit can be seen in Figure 6.

IV. DISCUSSION

Systems of Drude oscillators coupled together by dipole interactions are described by a quadratic Hamiltonian that can be diagonalized exactly by a normal-mode transformation. This can be viewed as an approximation to a system with the full Coulomb interaction of charges. The recent rise in interest in Drude oscillators has motivated us to study the properties of this basic quantum system without recourse to the dipole approximation. Several striking differences arise.

First, the Hamiltonian is not exactly diagonalizable,

and all bosonic number states contribute to the wavefunction. Even so, convergence of truncated calculations appears to be systematic, with errors decaying as $1/d$. Second, the correlation energy of Drude oscillator dimers is a defined and finite quantity at all separations.

Unlike in the dipole-approximation, there are mean-field effects beyond zeroth-order, closely corresponding to orbital relaxation effects in HF theory, and leading to a description of induction. The length-scale of this effect is governed by the radial extent of the monomer ground state, $\sqrt{\hbar}/(\mu\omega)$. Although we have not explored this here, the Drude parameters could be fitted to reproduce this length-scale correctly.

We note that the natural perturbation expansion, with the non-interacting system forming the zeroth-order Hamiltonian, converges rapidly and smoothly. RPA, which is exact in the dipole approximation, correctly returns the very long-range form of the potential, but is less accurate at short range. Correcting for single-excitation effects, RPA has an accuracy between that of PT2 and PT3 at short range.

V. SUMMARY

Drude oscillators offer a minimal and incredibly useful model for quantum mechanical charge fluctuations.

Here we investigate the exact nature of the interaction between pairs of Drude oscillators, and show that without the dipole approximation, they produce an accurate model of correlation effects at all separations of rare-gas atoms. The model also provides a qualitatively accurate description of induction interaction which is completely absent in dipole approximation. It appears that a more accurate parametrization scheme may also be able to describe induction effects quantitatively. We find that RPA does not provide a very accurate estimate of the binding energy, despite being exact in the dipole approximation. However, RPA with a self-consistently optimized ground state might perform better. The surprisingly rapid convergence of perturbation theory is another key result. In summary, this study sets out benchmark results against which other estimating the accuracy of other, more approximate theories can be judged.

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²² The situation for the exact interaction in the dipole approximation is actually a little more complicated, because at very small distances the ground state disappears altogether, when the normal-mode transformation produces one oscillator mode with negative force constant.

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