

Effective Hamiltonians for motions with disparate time scales: The quantum shell model and the classical statistical shell model

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The shell model of atomic polarizability is generalized to include a statistical distribution of shell states for each instantaneous configuration of the cores. Effective Hamiltonians for motions of the cores are derived for both quantum and classical descriptions of the shells. This extends the shell model into a formalism useful for molecular dynamics. The fluctuations of the shell positions account for London dispersion interactions. The resulting equations may also have applications to other systems containing motions with disparate time scales.

I. INTRODUCTION

In molecular dynamics and molecular mechanics simulations, one usually replaces the electrons by springs, atomic charges, and van der Waals interactions, with the parameters chosen to fit some selection of properties.¹ Despite many successes, it is clear that such rigid-ion descriptions do not describe the response to external electric fields, such as polarizability, dielectric relaxation, piezoelectricity,² hyperpolarizabilities, and dynamic polarization effects arising from the high electric fields present in the crystal. Such difficulties with the rigid-ion model are manifest in the lattice dynamics of ionic systems. For example, the splitting of the longitudinal and transverse optical modes in alkali halides is incorrect.³⁻⁶

A simple model for including polarization effects in molecular mechanics is the isotropic shell model,³⁻⁵ based on the classical Drude model,^{7,8} where each atom is described in terms of two components: the core and the shell. The shell is connected to its core by an isotropic harmonic spring,

$$\delta E = \frac{1}{2}k(\delta R)^2, \quad (1a)$$

$$k = \frac{s^2}{\alpha}, \quad (1b)$$

where δR is the displacement of the shell from its core, α is the atomic polarizability, s is the shell charge, and k is the spring constant. The shell then interacts with its core via the spring and with all other species via electrostatic interactions.³⁻¹⁰ The shell model has proved adequate for static crystal properties, including calculation of phonon dispersion curves,⁹⁻¹³ dielectric susceptibility,² and piezoelectric tensors.² However, fitting such a model to experimental data often leads to unphysical parameters.^{6,12,13}

For dynamical simulations there are two choices for how to handle the shell coordinates. One is to assign zero mass to the shell. In this case the shell positions change adiabatically with motions of the cores but kinetic energy effects are ignored. The other is to use finite mass. Adjusting the mass so that the shell vibrations correspond to typical (plasmon) excitation energies (5–20 eV) leads to very high frequencies for the shell motion and a concomi-

tant decrease in the time step for dynamical simulations by factors of 10^3 or more. Moreover, the shell motion should be quantized since the masses are similar to those of the electron.

Here we develop an analytic treatment of the shell model that renders it suitable for Monte Carlo and molecular dynamics simulations at any temperature. Our approach is based on the Drude model,^{7,8} which treats the atoms as isotropic, three-dimensional harmonic oscillators. This model was adapted by London,¹⁴ with only minor modifications, to describe quantum mechanical dispersion forces.

Since the cores are 10^3 – 10^5 times more massive than the shells, we consider them fixed during shell vibrations, i.e., we separate the shell and core motions. The shells equilibrate to the instantaneous positions of the cores according to statistical mechanical theory. The application of statistical mechanics is appropriate, since the nonlinear coupling between shell modes leads to energy flow and a statistical distribution of states. We then find the effective core Hamiltonian by “integrating out” the shell fluctuations with the help of classical or quantum statistical mechanical theory. The resulting effective Hamiltonian has two components. The first represents the energy due to the shells adopting the minimum energy position for any given core configuration. The second accounts for fluctuations, zero-point and excited-state motion in the quantum case and thermal fluctuations in the classical case.

II. THEORY

We assume the shells are in thermal equilibrium with a bath at the average temperature of the cores and perform our calculations for the constant N , V , and T canonical ensemble. We then write the effective core Hamiltonian as the core kinetic energy K_{core} plus the canonical shell Helmholtz free energy,

$$H_{\text{eff}} = K_{\text{core}} + A = K_{\text{core}} - \frac{\ln Q_s}{\beta}, \quad (2)$$

where $\beta = 1/k_B T$. This effective Hamiltonian depends only on core positions, since the shell positions are integrated out in the calculation of Q_s .

Basically we assume that the shells move much more rapidly than the cores, so they can re-equilibrate instantaneously as the cores move. In the low temperature quantum case, the shell modes are generally in their ground states (excitation energies are ~ 10 eV). This effective core Hamiltonian is then used in classical Monte Carlo or molecular dynamics simulations of the core motion, where the shell can be treated by either classical or quantum mechanics.

We start with a quadratic expansion of the shell Hamiltonian about the core positions. That is, we treat the shells as coupled, statistical harmonic oscillators. This assumption is usually valid since the core-shell interaction is much larger than the electrostatic couplings and the shell displacements are small. The resulting effective Hamiltonian for the cores is not at all quadratic and clearly contains many-body effects.

A. The shell Hamiltonian

The first step in integrating out the shell coordinates $\{\mathbf{r}_j; j=1, \dots, N\}$ is to expand the total energy of the system $E(\{\mathbf{R}_i; \{\mathbf{r}_j\})$, about the core coordinates $\{\mathbf{R}_i; i=1, \dots, N\}$ to quadratic order,

$$E(\{\mathbf{R}_i; \{\mathbf{r}_j\}) = E_0(\{\mathbf{R}_i\}) + \sum_{i=1}^N \mathbf{dr}_i \left(\frac{\partial E}{\partial \mathbf{r}_i} \right)_{\mathbf{r}_i=\mathbf{R}_i} + \frac{1}{2} \sum_{i,j=1}^N \mathbf{dr}_i \mathbf{dr}_j \left(\frac{\partial^2 E}{\partial \mathbf{r}_i \partial \mathbf{r}_j} \right)_{\mathbf{r}_i=\mathbf{R}_i, \mathbf{r}_j=\mathbf{R}_j}, \quad (3)$$

where $\mathbf{dr}_i = \mathbf{r}_i - \mathbf{R}_i$ is a small displacement of the shell from the position of the core and E_0 is the ion energy (including all interactions independent of \mathbf{dr}_i). We assume that $\langle \mathbf{r}_i \rangle \approx \mathbf{R}_i$, so that $\|\mathbf{dr}_i\|$ is small.

Rewriting Eq. (3) in tensor notation, again ignoring higher order terms, leads to

$$E(\{\mathbf{R}_i; \{\mathbf{r}_j\}) = E_0 + \mathbf{dr} \mathbf{E}' + \frac{1}{2} \mathbf{dr} \mathbf{E}'' \mathbf{dr}, \quad (4)$$

where $\mathbf{E}' \equiv \nabla_{\mathbf{r}} E$, $\mathbf{E}'' \equiv \nabla_{\mathbf{r}} \nabla_{\mathbf{r}} E$, \mathbf{dr} is the $3N$ vector of differential shell coordinates, and \mathbf{dr} is the transpose of \mathbf{dr} . From Eq. (4) the condition for equilibrium is

$$\mathbf{E}' + \mathbf{E}'' \cdot \mathbf{dr}_e = 0$$

or

$$\mathbf{dr}_e = -(\mathbf{E}'')^{-1} \mathbf{E}'. \quad (5)$$

To eliminate the linear term in Eq. (4), we define $\mathbf{y} = \mathbf{dr} - \mathbf{dr}_e$ as the displacement from equilibrium, leading to

$$E(\{\mathbf{R}_i; \{\mathbf{y}_j\}) = E_e + \frac{1}{2} \mathbf{y} \mathbf{E}'' \mathbf{y}, \quad (6)$$

where

$$E_e = E_0 - \frac{1}{2} \mathbf{E}' (\mathbf{E}'')^{-1} \mathbf{E}'$$

is the energy with all shells at equilibrium ($\mathbf{y}=0$). Therefore, the shell Hamiltonian is

$$H_s = \sum_{j=1}^N \frac{\mathbf{p}_j^2}{2m_j} + E(\{\mathbf{R}_i; \{\mathbf{r}_j\}), \quad (7)$$

where \mathbf{p}_j and m_j are the momentum and the mass of the shell, $j=1, \dots, N$.

B. The core effective Hamiltonians (H_{eff})

1. The classical statistical shell model

We now proceed to use classical statistical mechanics to integrate out the shell coordinates. This leads to an effective Hamiltonian of the form (2), depending only on \mathbf{R}_i .

The classical partition function for the shell coordinates is

$$Q_c(\{\mathbf{R}_i\}) = \frac{1}{h^{3N}} \int e^{-\beta H_s(\{\mathbf{R}_i; \{\mathbf{r}_j\})} d\mathbf{p}_1 \cdots d\mathbf{p}_N d\mathbf{r}_1 \cdots d\mathbf{r}_N \\ = \frac{1}{h^{3N}} \int e^{-\beta(E_e + \frac{1}{2} \mathbf{y} \mathbf{E}'' \mathbf{y} + \sum_{i=1}^N \mathbf{p}_i^2 / 2m_i)} \prod_{i=1}^N d\mathbf{p}_i d\mathbf{r}_i. \quad (8)$$

We simplify the integrand by diagonalizing the Hessian matrix \mathbf{E}''

$$\mathbf{E}'' \mathbf{X} = \mathbf{X} \mathbf{\Lambda} \quad (9)$$

where $\mathbf{\Lambda}$ is the matrix of eigenvalues of \mathbf{E}'' and \mathbf{X} is the matrix of eigenvectors. Thus Eq. (6) reduces to

$$E(\{\mathbf{R}_i; \{\mathbf{r}_j\}) = E_e + \frac{1}{2} \mathbf{y} \mathbf{E}'' \mathbf{y} = E_e + \frac{1}{2} \tilde{\mathbf{X}} \mathbf{\Lambda} \mathbf{X}. \quad (10)$$

Substituting Eq. (10) into Eq. (8), we obtain

$$Q_c(\{\mathbf{R}_i\}) = \frac{1}{h^{3N}} \left[\prod_{i=1}^N \left(\frac{2\pi m_i}{\beta} \right)^{3/2} \right] e^{-\beta E_e} \\ \times \int e^{-\frac{1}{2} \beta \tilde{\mathbf{X}} \mathbf{\Lambda} \mathbf{X}} \prod_{i=1}^N d\mathbf{X}_i. \quad (11)$$

The integrand in Eq. (11) is

$$\int e^{-\frac{1}{2} \beta \tilde{\mathbf{X}} \mathbf{\Lambda} \mathbf{X}} \prod_{i=1}^{3N} d\mathbf{X}_i = \prod_{i=1}^{3N} \sqrt{\frac{2\pi}{\beta \lambda_i}} = \left(\frac{2\pi}{\beta} \right)^{3N/2} (\det \mathbf{E}'')^{-1/2}, \quad (12)$$

including the determinant of \mathbf{E}'' . This leads to

$$\ln Q_c = \gamma_c - \beta E_e - \frac{1}{2} \ln(\det \mathbf{E}''), \quad (13)$$

where

$$\gamma_c = -3N \ln h + \frac{3}{2} \sum_{i=1}^N \ln \left(\frac{2\pi m_i}{\beta} \right) + \frac{3N}{2} \ln \left(\frac{2\pi}{\beta} \right)$$

represents all the factors in Eq. (13) independent of the core configuration. Thus the effective Hamiltonian, H_{eff} , for motion of the cores, Eq. (2), becomes

$$H_{\text{eff}} = K_{\text{core}} + A(\{\mathbf{R}_i; \{\mathbf{P}_i\}) \\ = \sum_{i=1}^N \frac{\mathbf{P}_i^2}{2M_i} - \frac{1}{\beta} \ln Q_c \\ = \sum_{i=1}^N \frac{\mathbf{P}_i^2}{2M_i} - \frac{1}{\beta} \gamma_c + E_e + \frac{1}{2\beta} \ln(\det \mathbf{E}''), \quad (14)$$

where M_i is the core mass and the dependence on the shell coordinates has been successfully removed. Note that the factor γ_c is independent of the core configuration. The result is a core effective Hamiltonian that depends only on core positions \mathbf{R}_i and momenta \mathbf{P}_i . We refer to this as the classical statistical shell model or CSSM.

As the temperature goes to zero, the CSSM Hamiltonian Eq. (14) reduces to the usual assumption that the shells remain in their minimum energy configuration. The last term in Eq. (14) is the entropy term of classical statistical mechanics. It is proportional to temperature, a classical effect, and is related to the Hessian matrix (second derivatives) of the energy with respect to shell positions. Note that the effective Hamiltonian contains many-body terms introduced by the determinant of the Hessian. That is, statistical averaging of a manifestly pairwise potential has produced many-body effects.

2. The quantum shell model

The vibrational frequencies from oscillations of the shell coordinates correspond to the frequencies of collective modes for the electrons. This will typically be in the range of 5–20 eV. With typical shell-core force constants this leads to a shell mass near that of a free electron. Thus the shell motions should be quantized. If the shells are in equilibrium with a reservoir at temperature T , the average core temperature, the partition function from quantum statistical mechanics is

$$Q_q = \text{Tr}(e^{-\beta H_s}). \quad (15)$$

Diagonalizing the mass weighted Hessian $\mathbf{E}''_{m} = \mathbf{M}^{-1/2} \mathbf{E}'' \mathbf{M}^{-1/2}$ leads to

$$E(\{\mathbf{R}_i\}; \{\mathbf{r}_j\}) = E_e + \frac{1}{2} \tilde{\mathbf{X}}_m \mathbf{A}_m \mathbf{X}_m, \quad (16)$$

where \mathbf{M} is the diagonal matrix of the shell masses, $\mathbf{M}_{ij} = \delta_{ij} m_i$ and $\mathbf{X}_m = \sqrt{\mathbf{M}} \mathbf{X}$. All symbols are defined as in the classical case, with subscript m indicating mass weighted coordinates. The eigenvalue is $\lambda_{m_i} = (2\pi\nu_i)^2$, where ν_i is the vibrational frequency of the normal mode.

Using Eq. (16) in Eq. (7), the quantum shell Hamiltonian becomes

$$H_s = E_e + \frac{1}{2} \sum_{i=1}^{3N} (\mathbf{X}_{m_i}^2 \lambda_{m_i} + \dot{\mathbf{X}}_{m_i}^2) \quad (17)$$

with $3N$ harmonic oscillators. Substituting Eq. (17) into (15) and letting H_i be the Hamiltonian of oscillator i , the partition function Q becomes¹⁵

$$Q_q = e^{-\beta E_e} \prod_{i=1}^{3N} \text{Tr} e^{-\beta H_i} = e^{-\beta E_e} \sum_{n>0} e^{-\beta E_n}, \quad (18)$$

where $E_n = \sum_{i=1}^{3N} (n_i + \frac{1}{2}) h\nu_i$. Substituting E_n into Eq. (18), we obtain

$$Q_q = e^{-\beta E_e} \prod_{i=1}^{3N} \frac{e^{-\frac{1}{2}\beta h\nu_i}}{1 - e^{-\beta h\nu_i}}. \quad (19)$$

Thus the effective Hamiltonian for motion of the cores is

$$H_{\text{eff}}^{\text{core}} = K_{\text{core}} + A(\{\mathbf{R}_i\})$$

$$\begin{aligned} &= K_{\text{core}} - \frac{1}{\beta} \ln Q_q \\ &= \sum_{i=1}^N \frac{\mathbf{P}_i^2}{2M_i} + E_e + \sum_{i=1}^{3N} \left[\left(\frac{h\nu_i}{2} \right) + \frac{1}{\beta} \ln(1 - e^{-\beta h\nu_i}) \right] \end{aligned} \quad (20)$$

$$\sim \sum_{i=1}^N \frac{\mathbf{P}_i^2}{2M_i} + E_e + \sum_{i=1}^{3N} \left(\frac{h\nu_i}{2} \right) \quad (21)$$

$$= \sum_{i=1}^N \frac{\mathbf{P}_i^2}{2M_i} + E_e + \frac{h}{4\pi} \sum_{i=1}^{3N} \sqrt{\lambda_{m_i}}. \quad (22)$$

The λ_{m_i} in Eq. (22) is related to the vibration frequency of the shell modes which depends on the core coordinates. The core effective Hamiltonian, Eq. (20) or Eq. (22), is independent of shell coordinates. We refer to this as the quantum shell model or QSM.

In the step from Eq. (20) to Eq. (21), we neglect the last term since the shell frequency $h\nu_i$ is generally 5–20 eV while $1/\beta = 0.025$ eV at room temperature. Thus equation Eq. (21) or Eq. (22) describes the shells as remaining in the ground quantum state during motions of the cores and represents the zero-point vibration of the shells. This is clearly a quantum effect and, unlike the classical case, does not depend on temperature. In the classical limit, $h \rightarrow 0$ or $T \rightarrow \infty$, equation Eq. (20) reduces to the classical limit Eq. (14).

III. CLASSICAL MOLECULAR DYNAMICS SIMULATIONS

The effective Hamiltonian [Eq. (22) for QSM or Eq. (14) for CSSM] is used for classical molecular dynamics simulations of the core motions. This requires taking derivatives of H_{eff} with respect to core coordinates to obtain forces. The presence of the shell Hessian or its eigenvalues in the effective Hamiltonian complicates the equations since the derivatives of these quantities must be updated at every time step. There are a number of approaches to making this practical, some of which we mention below.

The Hessian for shell motions is dominated by large diagonal components due to the shell–core interactions; hence, it is expected that the remainder of the Hessian (which depends on various dipole–dipole interactions) could be treated as a perturbation and evaluated less frequently than every time step.

For CSSM the \mathbf{E}'' matrix appears in the log of the determinant in Eq. (14). Using chain rules,

$$\begin{aligned} \frac{\partial H_{\text{eff}}}{\partial \mathbf{R}_k} &= \frac{\partial E_0}{\partial \mathbf{R}_k} + \frac{\partial H_{\text{eff}}}{\partial \mathbf{E}'_i} \frac{\partial \mathbf{E}'_i}{\partial \mathbf{R}_k} + \frac{\partial H_{\text{eff}}}{\partial \mathbf{E}''_{ij}} \frac{\partial \mathbf{E}''_{ij}}{\partial \mathbf{R}_k} \\ &\quad + \frac{\partial \ln(\det \mathbf{E}'')}{\partial \mathbf{E}''_{ij}} \frac{\partial \mathbf{E}''_{ij}}{\partial \mathbf{R}_k}, \end{aligned} \quad (23)$$

where

$$\frac{\partial \ln(\det \mathbf{E}'')}{\partial \mathbf{E}''_{ij}} = (\mathbf{E}''^{-1})_{ij} \quad (24)$$

and the subscripts in the partial derivatives are summed over $3N$ coordinates. Thus we obtain an analytic form for the forces on the cores. This requires evaluating the first derivative of the core effective Hamiltonian (third derivatives of the energy) which must be updated at each time step of the dynamics. To avoid evaluating matrix inversions at every time step, a geometric series can be used to update the numerical value of $(\mathbf{E}'')^{-1}$.

$$\begin{aligned} (\mathbf{E}'' + \epsilon)^{-1} &= \{\mathbf{E}'' [1 + (\mathbf{E}'')^{-1} \epsilon]\}^{-1} \\ &= \{1 - (\mathbf{E}'')^{-1} \epsilon + [(\mathbf{E}'')^{-1} \epsilon]^2 - \dots\} \\ &\quad \times (\mathbf{E}'')^{-1}, \end{aligned} \quad (25)$$

where ϵ is a small increment, $\|\epsilon\| \ll 1$. In practical applications of Eq. (25):

$$\epsilon = \mathbf{E}''(t + \Delta t) - \mathbf{E}''(t).$$

After iterative updating for several steps, one would invert the matrix \mathbf{E}'' explicitly to recover the exact $(\mathbf{E}'')^{-1}$. The time for full diagonalization and matrix inversion is proportional to N^3 while matrix multiplication required in Eq. (25) is also $O(N^3)$, but we expect the coefficient for the later process to be smaller.

For QSM we also use the chain rule to obtain the first derivative of the effective Hamiltonian

$$\begin{aligned} \frac{\partial H_{\text{eff}}}{\partial \mathbf{R}_k} &= \frac{\partial E_0}{\partial \mathbf{R}_k} + \frac{\partial H_{\text{eff}}}{\partial \mathbf{E}'_{m_i}} \frac{\partial \mathbf{E}'_{m_i}}{\partial \mathbf{R}_k} + \frac{\partial H_{\text{eff}}}{\partial \mathbf{E}''_{m_{ij}}} \frac{\partial \mathbf{E}''_{m_{ij}}}{\partial \mathbf{R}_k} \\ &\quad + \frac{\partial H_{\text{eff}}}{\partial \lambda_{m_i}} \frac{\partial \lambda_{m_i}}{\partial \mathbf{E}''_{m_{ij}}} \frac{\partial \mathbf{E}''_{m_{ij}}}{\partial \mathbf{R}_k}. \end{aligned} \quad (26)$$

Here the derivative of λ_{m_i} can be written as

$$\frac{\partial \lambda_{m_i}}{\partial \mathbf{E}''_{m_{kj}}} = \mathbf{X}_{m_{ki}} \mathbf{X}_{m_{jl}} = \frac{\partial \lambda_{m_i}}{\partial \mathbf{E}''_{m_{jk}}}, \quad (27)$$

where $\mathbf{X}_{m_{kl}}$ is the k th element of mass weighted eigenvector l . Equation (27) involves diagonalization of the Hessian matrix \mathbf{E}''_m . Explicit diagonalization at every time step might be avoided using perturbation theory. Thus if \mathbf{E}''_m is nondegenerate, the perturbation theory for $\mathbf{E}''_m = \mathbf{M}_0 + \mathbf{M}_1$ takes the form,¹⁶

$$\begin{aligned} \lambda_{m_i} &= \lambda_{m_i}^0 + \langle \mathbf{x}_{m_i}^0 | \mathbf{M}_1 | \mathbf{x}_{m_i}^0 \rangle + \sum_{j \neq i} \frac{|\langle \mathbf{x}_{m_j}^0 | \mathbf{M}_1 | \mathbf{x}_{m_i}^0 \rangle|^2}{\lambda_{m_i}^0 - \lambda_{m_j}^0}, \\ \mathbf{x}_{m_i} &= \mathbf{x}_{m_i}^0 + \sum_{k \neq i} \mathbf{x}_k^0 \left[\frac{\langle \mathbf{x}_{m_k}^0 | \mathbf{M}_1 | \mathbf{x}_{m_i}^0 \rangle}{\lambda_{m_i}^0 - \lambda_{m_k}^0} \left(1 - \frac{\langle \mathbf{x}_{m_i}^0 | \mathbf{M}_1 | \mathbf{x}_{m_i}^0 \rangle}{\lambda_{m_i}^0 - \lambda_{m_k}^0} \right) \right. \\ &\quad \left. + \sum_{j \neq i} \frac{\langle \mathbf{x}_{m_k}^0 | \mathbf{M}_1 | \mathbf{x}_{m_j}^0 \rangle \langle \mathbf{x}_{m_j}^0 | \mathbf{M}_1 | \mathbf{x}_{m_i}^0 \rangle}{(\lambda_{m_i}^0 - \lambda_{m_k}^0)(\lambda_{m_i}^0 - \lambda_{m_j}^0)} \right], \end{aligned} \quad (28)$$

where $\lambda_{m_i}^0$ and $\mathbf{x}_{m_i}^0$ are the i th element of the zeroth order eigenvalue and eigenvector of \mathbf{E}'' , respectively. The \mathbf{x}_{m_i} should be normalized to unity at each step.

In analogy with Eq. (25), perturbation theory can be used to update the eigenvalues and eigenvectors. This al-

lows λ_{m_i} and \mathbf{x}_{m_i} to be updated iteratively without having to diagonalize the matrix. Again, the matrix should be diagonalized after several steps to recover the exact eigenvalues and eigenvectors.

IV. DISCUSSION

A. Quantum shell model (QSM)

In order to characterize the polarization of atoms in materials (an effect that originates from electron motions), the shell model is introduced into the potential. The shell vibration states should be quantized; hence, we expect the outcome from classical mechanics descriptions to be in considerable error. The quantum shell model allows molecular dynamics and Monte Carlo simulations (for those materials where the simple shell model description of forces is valid).

A bonus with QSM is that the zero-point motion of the shells in Eq. (22) includes the fluctuating dipoles responsible for the London dispersion or van der Waals attractions ($-C/R^6$). This is a fluctuation-induced force resulting from instantaneous dipole-dipole interactions. To illustrate this, consider the general Eq. (22), for two spherical neutral particles a and b . The interaction potential becomes

$$\begin{aligned} E &= \frac{s_a s_b}{|\mathbf{R}|} + \frac{s_a s_b}{|\mathbf{r}_b - \mathbf{r}_a|} - \frac{s_a s_b}{|\mathbf{R} - \mathbf{r}_a|} - \frac{s_a s_b}{|\mathbf{r}_b|} + \frac{1}{2} k_a r_a^2 \\ &\quad + \frac{1}{2} k_b (r_b - \mathbf{R})^2 \end{aligned} \quad (29)$$

where $\mathbf{0}$, \mathbf{R} , \mathbf{r}_a , and \mathbf{r}_b are the position vectors for the core_{*a*}, core_{*b*}, shell_{*a*}, and shell_{*b*} with respect to core_{*a*}. k_i is the spring constant and $-s_i$ is the shell charge. Thus the Hessian matrix takes the form

$$\mathbf{E}'' = \begin{bmatrix} k_a & 0 & 0 & \frac{s_a s_b}{R^3} & 0 & 0 \\ 0 & k_a & 0 & 0 & \frac{s_a s_b}{R^3} & 0 \\ 0 & 0 & k_a & 0 & 0 & -\frac{2s_a s_b}{R^3} \\ \frac{s_a s_b}{R^3} & 0 & 0 & k_b & 0 & 0 \\ 0 & \frac{s_a s_b}{R^3} & 0 & 0 & k_b & 0 \\ 0 & 0 & -\frac{2s_a s_b}{R^3} & 0 & 0 & k_b \end{bmatrix}. \quad (30)$$

The eigenvalues can be found analytically, with the last term in H_{eff} , Eq. (22), becoming

$$\frac{\hbar}{2} (3\nu_a + 3\nu_b) - \frac{3\hbar}{2} \left(\frac{\nu_a \nu_b}{\nu_a + \nu_b} \right) \alpha_a \alpha_b \left(\frac{1}{R^6} \right) + O\left(\frac{1}{R^{12}} \right), \quad (31)$$

where $v_a = \frac{1}{2\pi} \sqrt{k_a/m_a}$, $v_b = \frac{1}{2\pi} \sqrt{k_b/m_b}$, and α is defined as in Eq. (1b). The dispersion energy is the difference between the zero-point energy of the isolated particles and that of the interacting particle. The result is consistent with the dispersion energy derived from the Drude model for two particles, each harmonically and isotropically bound to its individual equilibrium position.^{7,8}

For two identical atoms the London dispersion energy from Eq. (31) is

$$E_{\text{disp}}(R) \sim -C_6 \left(\frac{1}{R^6} \right), \quad (32a)$$

where

$$C_6 = \frac{3 s \alpha^{3/2}}{4 m^{1/2}} \quad (\text{in atomic units}). \quad (32b)$$

With three spherical neutral particles, the quantum formula Eq. (22) leads to a sum of pair terms as in Eq. (32) plus the Axilrod–Teller correction,¹⁷

$$\delta E_{\text{A-T}}(R) = C_{\text{A-T}} \frac{(1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k)}{(R_{ij} R_{jk} R_{ki})^3}, \quad (33a)$$

where

$$C_{\text{A-T}} = \frac{9 s \alpha^{5/2}}{16 m^{1/2}} \quad (\text{in atomic units}). \quad (33b)$$

Here θ_i , θ_j , θ_k are the three angles of the triangle with sides R_{ij} , R_{jk} , and R_{ki} . This corresponds to the first order correction for three-body potentials. These results demonstrate that, for the simplest cases of two or three particles at moderate separation, equation Eq. (22) predicts the familiar $1/R^6$ and Axilrod–Teller terms.^{14,17}

These results [Eq. (32) and Eq. (33)] from Eq. (22) are limiting cases, presented here to reveal the validity of this formalism. Unlike the Drude model, which constructs the potential with sets of pairwise interactions, the effective Hamiltonian obtained via the statistical mechanical approach clearly contains the many-body interactions. Although analytic derivation of the formulas for the higher order interactions (e.g., four or five body interactions) is rather complex and sometimes impractical, the numerical calculations are straightforward. The number of particles to be included in the simulations can be thousands, depending on the system of interest. Furthermore, the derivation of the effective Hamiltonian puts no restrictions on the distance range where the formula applies. Thus the interaction potential can be evaluated numerically at intermediate separations. However, our Hamiltonians do not take into account the overlap of the electron clouds or the exchange interactions (Pauli principle).

For molecular systems the shell parameters [s and α in Eq. (1b)] can be determined by fitting to molecular polarizabilities. Kim and Gordon¹⁸ investigated the resulting London dispersion interactions for closed-shell atoms, ions, and molecules and compared with C_6 values measured from gas-phase scattering experiments. The “effective number of electrons” responsible for the dispersion force, was determined by fitting with experimental C_6 data.

This oscillator approach describes reasonably well the various charge–dipole and dipole–dipole interactions. The v_i for Ar determined by $h v_i = \frac{4}{3} (c_6 / \alpha^2)$ is about 19 eV, which shows the necessity for quantization of the shell model. Kim and Gordon chose the shell mass as $s m_e$ (where m_e is the electron mass) so that the shell charge could be uniquely determined from Eq. (32b) (given the C_6 coefficient and the polarizability). However, the shell mass can be treated as an extra parameter since the oscillating electron model does not enforce the exact mechanism of individual electron motion. We suggest choosing it to fit the strongly allowed electronic transitions or plasmon modes.

The shell model, proposed by Dick and Overhauser³ and used extensively thereafter, does not take into account the kinetic energy of the shells. Thus it ignores the high frequency zero-point motion of the shells. Generally the shell mass is assigned to zero, which implies no force exerted on the shells when solving Newton’s equations of motion in atomic simulations. This may account for the nonphysical parameters^{6,12,13} obtained with this model. Naive inclusion of the shell mass into standard MD simulations would not only require time steps 10^3 shorter (light mass), but would also lead to incorrect results, since neither quantum effects nor statistical averaging is included.

Since the London dispersions are already included in the quantum formula, classical dynamics simulations using Eq. (22) should *not* include these terms in the explicit nonbonded potential [$(E_0$ of Eq. (3)]. Thus only the short range repulsions (Pauli orthogonality) and electrostatic interactions would be included. Since the short range repulsions can be calculated easily from quantum mechanical wave functions (e.g., Hartree–Fock) that *do not* include London dispersion, this might simplify derivation of the potentials.

The effective Hamiltonians developed here are not restricted to the simple isotropic harmonic shell model in Eq. (1). They could be used with more general shell formulations involving shells at bond midpoints or other interstitial position¹⁹ or a nonisotropic force constant matrix.

With either the QSM or the CSSM formula, the second order corrections for two neutral particles leads to terms of the order of $1/R^{12}$. This differs from the usual result at large R where⁸

$$E_{\text{London}} = -\frac{C_6}{R^6} - \frac{C_8}{R^8} - \frac{C_{10}}{R^{10}}$$

(for neutral spherical particles). The origin of this discrepancy is the harmonic expansion in Eq. (3), which neglects multipole interactions higher than dipole–dipole. For example, the $1/R^8$ term comes from a dipole–quadrupole interaction that contributes in second order perturbation theory. The appropriate perturbation is cubic in $d r_i$ which is not present in Eq. (3). However, for most of the systems of interest, the harmonic description is appropriate.

B. Classical statistical shell model (CSSM)

Using the classical formula (14) to consider the interactions of three atoms, the last term in the effective Hamil-

tonian Eq. (14) leads asymptotically to a sum of $1/R^6$ attractions [as in Eq. (32)], plus a three-body term similar to Eq. (33)

$$E(R) \sim \text{const} - 4 \left(\frac{3 \alpha^2}{4 \beta} \right) \left[\left(\frac{1}{R_{ij}^6} \right) + \left(\frac{1}{R_{jk}^6} \right) + \left(\frac{1}{R_{ki}^6} \right) \right] + \frac{16}{3} \left(\frac{9 \alpha^3}{16 \beta} \right) \frac{(1 + 3 \cos \theta_i \cos \theta_j \cos \theta_k)}{(R_{ij} R_{jk} R_{ki})^3} \quad (34)$$

However, for CSSM the presence of β leads to a linear dependence on temperature. This temperature dependence is a well known classical result²⁰ whereas London dispersion is a quantum effect.¹⁴ This suggests that in using Eq. (14), the β in the last terms must be fixed in some way so as to approximate the quantum result. An additional problem with CSSM is that the coefficients of the two-body and three-body corrections in Eq. (34) have different proportions than in the quantum case. This is to be expected since the $\ln(\det \mathbf{E}'')$ in Eq. (14) is not proportional to the sum of the square roots of the eigenvalues of \mathbf{E}''_m involved in Eq. (22). Even so, Eq. (14) may be useful when the zero-point energy of the faster motion to be integrated out is insignificant compared to the average energy. In this case many of the higher modes will be activated and the system should exhibit a statistical population of states. At high temperature when the classical limit is valid, (e.g., motions in polymer chains) Eq. (14) might provide an efficient way to implement statistical averaging. It might also be a useful approximation when the evaluation of eigenvalues from quantum case (which involves diagonalization of the Hessian matrix) is not practical.

C. Other systems

The quantum H_{eff} in Eq. (22), and the classical statistical H_{eff} in Eq. (14), can be used for other systems containing light particles interacting with much heavier particles. For example, in the molecular dynamics of molecules or solids, particularly of organic polymers and biopolymers, the modes involving hydrogen have frequencies large compared to thermal energies. Thus they should be described in the zero quantum state, with a spatial distribution independent of temperature, and would not contribute to the specific heat. However classical dynamics leads to temperature dependent motions and a full contribution to the specific heat. The quantum or classical effective Hamiltonians (22) or (14) could be used to eliminate the H motions from the dynamical description of the heavy atom coordinates. This should be much more accurate than the common approach of implicitly including the hydrogens into the adjacent heavy atoms (united atoms).²¹

For molecules and crystals containing positronium, the QSM equation would allow the positronium motions to be quantized, providing a means for efficiently simulating the dynamics.

In addition, analogous quantum or classical statistical effective Hamiltonians could be derived for other systems containing motions with disparate time scales (e.g., tor-

sions of polymer chains, librations in molecular crystals, and diffusion in solids).

V. COMPARISON TO OTHER METHODS

Effective Hamiltonians involving an analytic description of *both* shell and core coordinates have previously been derived for shell models of solids.²² These treatments involve additional simplifying assumptions about the shell-core and core-core interactions and even about the dimensionality of the system. Our approach is distinct from these previous analytic approaches in that we treat only the shells analytically. Thus we leave the evaluation of the core properties as a numerical task to be handled with standard numerical programs.

The statistical description in shell model should have advantages over analytic integration of a harmonic approximation to the motion of the light particles.²³ For example, pure harmonic approximations do not allow energy flow between oscillators, thereby preventing the system from equilibrating. Moreover, the classical harmonic oscillator without statistical averaging overestimates the position density at the classical turning points, whereas classical and quantum statistical mechanics predict Gaussian position densities.²⁴

The harmonic shell approximation has been found inadequate for the treatment of oxides and chalcogenides with ferroelectric soft modes (where nonlinear polarization response is important).²⁵ It is possible that, with an anisotropic k matrix, the many-body effects implicit in the QSM or CSSM formulations would abrogate these difficulties, however this remains to be investigated.

VI. CONCLUSIONS

We have provided a formalism for simulating motions with disparate time scales, with the focus on the simulation of polarization effects in molecules and solids. Using statistical mechanical theory, we have obtained analytic effective core Hamiltonians which include the effects of an ensemble of quantized shell coordinates (QSM) or of a classical statistical distribution (CSSM) on the motions of the cores. The QSM approach should provide an accurate description of electron fluctuations. For example, QSM automatically leads to London dispersion interactions.

These methods should also be useful for including the effects of light particles on the motions of heavier atoms, which are treated with classical molecular dynamics. This statistical approach, together with the suggested numerical techniques, should provide a means to efficiently incorporating rapid dynamical position fluctuations.

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