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The Wang–Landau sampling method is adapted to the calculation of quantum densities of states for fully coupled anharmonic systems. The accuracy of the method is illustrated against exact counting for two molecules with separable oscillators, namely, the Zundel complex $H_5O_2^+$ and the Na_{11} cluster. Application to the fully coupled naphthalene molecule ($C_{10}H_8$) reveals significant deviations in the finite temperature thermodynamical properties that are not captured by simple perturbation theory. There are no limitations in the size of the molecules that can be treated with this method. © 2008 American Institute of Physics. [DOI: 10.1063/1.2965905]

The density of states (DOS) is of primary importance in molecular and chemical physics. It readily provides information about the energetics and thermodynamics at equilibrium, and is also crucial for accurate spectroscopy. Beyond equilibrium, the processes of energy transfer, collisions, and fragmentations are connected to the DOSs through appropriate statistical theories such as Rice–Ramsperger–Kassel–Marcus. The determination of DOSs for multidimensional systems is a difficult task that has been satisfactorily solved only in very few cases. *Classical* DOSs can be accurately computed for anharmonic systems using a variety of approaches such as histogram reweighing,[1] transition matrix Monte Carlo (MC),[2] adiabatic switching,[3] or multicanonical ensemble simulations.[4,5] *Quantum* densities, on the other hand, are exactly known only in the very limited case of separable systems.[6,7]

For coupled anharmonic systems, the existing methods proposed so far are partly approximate. The accuracy of quantum corrections to the classical anharmonic densities[8,9] is generally difficult to assess. The more rigorous inverse Laplace transformation of the quantum partition function obtained, e.g., by quantum MC methods,[10] would be more appealing if not plagued by practical problems.[11] Along similar lines, several authors have proposed to estimate the microcanonical density from thermal (canonical) properties.[9,12,13]

Couplings between the various vibrational degrees of freedom can be expressed using the so-called Dunham expansion of the energy E in terms of the m quantum numbers $\{n\} \equiv (n_1, \ldots, n_m)$,

$$E = \sum_i h\nu_i\left(n_i + \frac{1}{2}\right) + \sum_{i \leq j} \chi_{ij}\left(n_i + \frac{1}{2}\right)\left(n_j + \frac{1}{2}\right), \quad (1)$$

where the harmonic frequencies and the anharmonic couplings have been denoted as ν_i and χ_{ij}, respectively. Such expansions have remained of limited and academic interest for polyatomic molecules until automatic perturbative approaches were recently implemented in modern electronic structure packages to obtain these coefficients.[14] Under reasonable validity assumptions of the Dunham expansion,[15] quantum densities and sums of states for the above expression of the energy can be estimated by MC sampling;[15,16] however, the standard MC procedure becomes inefficient for large m due to the difficulty in reducing the variance in high-dimensional sampling.[16] In this Communication, we show that the Wang–Landau (WL) method,[5] originally introduced for classical densities, is also very efficient for calculating accurate quantum DOSs of large nonseparable systems.[17] The WL method is a recursive algorithm in which the multicanonical weights are progressively constructed with increasing accuracy, eventually providing the DOS itself.

We denote by $\Omega(E)dE$ the number of vibrational states having energy E given by Eq. (1) within dE. The DOS Ω is obtained iteratively in the energy range of interest $[E_{\min}, E_{\max}]$ by performing a random walk in the space of quantum numbers $\{n\}$ according to the following rules. The current estimate of $\Omega(E)$ and the accumulating energy histograms are denoted as the functions $G(E)$ and $H(E)$, respectively. In practice, overflow problems are avoided by considering the logarithm $g(E) = \ln G(E)$ instead of G. Both functions g and H are initially set to 0 in the entire energy range. From the old vibrational state $\{n\}_{\text{old}}$, a new state $\{n\}_{\text{new}}$ is generated by collective displacement of all individual quantum numbers around their initial value $n_i^{(\text{old})}$,

$$n_i^{(\text{old})} \rightarrow n_i^{(\text{new})} = n_i^{(\text{old})} + \delta n_i. \quad (2)$$

Here δn_i is chosen as -1 with probability $p > 0$, $+1$ with the same probability p, and as 0 with probability $1 - 2p$. The same values taken for the -1 and $+1$ displacements stem from detailed balance requirements. Precise values for p were taken in the range of 4%–23% depending on the system and energy range covered. In the case where a negative number is generated for any particular n_i, then this number is kept to its initial value, which in this case would be 0.

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The new set $\{n\}_{new}$ of vibrational quantum numbers is used to compute the energy E_{new} of the system using Eq. (1). Denoting by E_{old} the energy corresponding to the previous set $\{n\}_{old}$, the new set is accepted with the probability

$$\mathrm{acc}(\{n\}_{old} \to \{n\}_{new}) = \min\left[1, \frac{\exp g(E_{old})}{\exp g(E_{new})}\right]. \quad (3)$$

If the set $\{n\}_{new}$ is accepted, then we update the corresponding histogram by 1, but we also increase the running estimate of g by some quantity $f > 0$,

$$H(E_{new}) \to H(E_{new}) + 1, \quad (4)$$

$$g(E_{new}) \to g(E_{new}) + f. \quad (5)$$

If the set $\{n\}_{new}$ was rejected, then the same procedure of Eqs. (4) and (5) applies but for the old number $\{n\}_{old}$ instead. If the new energy E_{new} lies beyond the energy boundaries E_{min} and E_{max}, then the new move is also rejected but H and g are updated at the old set.

As in the original WL method, detailed balance is strictly satisfied by the above procedure only asymptotically.[5] The smoothness of the histogram $H(E)$ is monitored from the deviation $\Delta(E) = [H(E) - \langle H \rangle]/\langle H \rangle$ around its average $\langle H \rangle$. As soon as $\Delta(E)$ goes below 90% for all energies E in the range $[E_{min}, E_{max}]$, or if the number of MC steps exceeds a given limit (here 2×10^6), then the histogram is reset to 0 and f is reduced by taking its square root. This procedure is repeated until f has reached the required accuracy, at which stage $G(E) = \exp g(E)$ provides our estimate for the quantum density of vibrational states. In the present work, 20 iterations on f were performed. However, because Eq. (1) is straightforward to calculate, we have found the method to be more accurate by averaging the final density $G(E)$ from several independent WL simulations.

Our first application concerns the proton bound water dimer, that is, the Zundel complex $H_5O_2^+$, for which accurate harmonic vibrational frequencies have been calculated recently by Sauer and Döbler at the CCSD(T) level.[18] This is yet a modest system ($m = 15$) but with a rather large spreading of its frequency distribution between the softest complex bending mode (172 cm^{-1}) and the hardest O–H stretching mode (3876 cm^{-1}). For this system, we chose the energy grain of the calculation to be 40 cm^{-1}. In order to describe more accurately the strong quantum fluctuations of the DOS at low energy, the WL simulation was performed in two separate overlapping energy windows covering the ranges of 0–0.3 and 0.12–2 eV, respectively. The probability p was taken as $p = 0.22$, yielding an average energy variation during each MC step of about 0.6 eV. The quantum DOS obtained using the WL method for the harmonic Zundel complex is compared in Fig. 1(a) with the results from the exact counting using the Beyer–Swinehart algorithm.[6]

For this benchmark system, our calculations are in remarkable agreement with the exact result in the entire energy range. At high energy, the smooth increase in the DOS is quantitatively reproduced by our method. More interestingly, in the low-energy regime, the quantum discretization of the DOS seen on the sharp and nonmonotonic fluctuations is also in very good agreement with the exact counting.
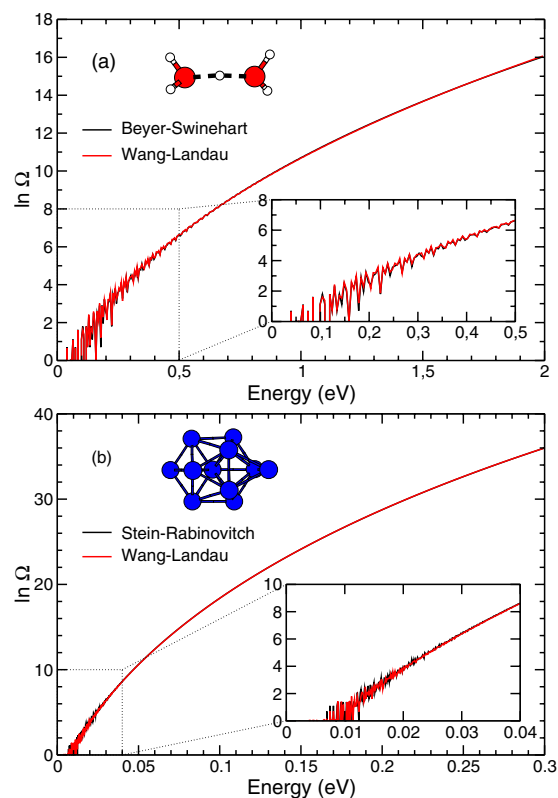

FIG. 1. (Color online) Quantum DOS of separable molecular systems obtained with the WL method or using the exact counting. (a) Harmonic model for the Zundel cation $H_5O_2^+$; (b) Na_{11} cluster with anharmonic but separable modes.

Next, the Na_{11} cluster was chosen to provide a case with a narrower distribution in vibrational frequencies. For this metallic system, the frequencies and anharmonicities were computed using density-functional theory (DFT) with the B3LYP/6-31+G(d) basis set, as implemented in the GAUSSIAN03 software package.[19] The cluster was chosen in the locally stable C_s minimum depicted in Fig. 1(b). Its vibrational frequencies lie in the range 18–134 cm^{-1}, with an average value of 76 cm^{-1}. They are explicitly given in Table I, along with the corresponding diagonal anharmonic coefficients χ_{ii}. The latter is essentially negative, and only important for the hardest eight modes. The WL calculations used an energy grain of 1 cm^{-1}, and the energy range was again split into two overlapping windows of 0–0.02 and 0.01–0.3 eV for a better accuracy. p was set to 10%, yielding an average energy change of about 10 meV/MC step.

The WL calculation was performed for the separable system ($\chi_{ij} = 0$ for all $i \neq j$). The quantum DOS of the Na_{11} cluster is shown in Fig. 1(b) against the exact results obtained with the Stein–Rabinovitch counting algorithm.[7] Here again the MC method successfully reproduces the reference data in the entire energy range, including at low energy where the state density is highly discretized. For this system, anharmonic effects are weak, and calculations performed after taking all χ_{ij} to zero also agree with the exact counting (results not shown).

The last system studied in this Communication is the naphthalene molecule ($C_{10}H_8$), for which the full set of frequencies and anharmonicity coefficients χ_{ij} have been re-

TABLE I. Harmonic frequencies and diagonal anharmonic coefficients obtained for the Na_{11} cluster at the B3LYP/6-31+G(d) level. All values are in cm^{-1}.

ν_i	χ_{ii}	ν_i	χ_{ii}	ν_i	χ_{ii}	ν_i	χ_{ii}
18.818	0.000	53.799	0.000	71.913	0.000	106.800	−0.055
32.955	0.000	60.077	0.000	78.240	0.000	111.761	−0.178
33.815	0.000	60.375	0.000	84.192	0.000	126.498	−0.085
38.445	0.000	65.806	0.000	86.702	0.000	129.262	−0.447
42.324	0.000	68.673	0.000	90.745	0.000	132.606	−0.270
43.793	0.000	70.272	0.000	95.511	−0.094	133.783	−0.514
45.206	0.000	71.206	0.000	106.584	−0.061		

cently obtained by Cané et al. using DFT at the B9-71/TZ2P level.[20] The WL calculations were performed in the energy range of 0–6 eV with a 20 cm^{-1} energy grain using the two overlapping energy windows of 0–0.3 and 0.15–6 eV. An appropriate value for the probability p was determined by considering first the separable system and getting the most efficient convergence to match the exact results in the whole energy range. The choice of $p=5\%$ leads to average energy changes of about 0.32 eV per MC move.

The quantum DOS of the naphthalene molecule are shown in Fig. 2 in the two separable cases of harmonic and anharmonic oscillators and for the fully coupled case. As was the case in our two benchmark examples, the DOS obtained for the separable systems with the WL sampling method agree well with the exact counting, for which the curves have been omitted in Fig. 2. The more numerous degrees of freedom of the naphthalene molecule ($m=48$) lead to rather smooth increasing variations of the densities with respect to the previous smaller systems. The effects of anharmonicities are emphasized in the inset of Fig. 2, where the state densities of the separable anharmonic and coupled anharmonic systems are represented relative to the harmonic reference.

Accounting for diagonal anharmonicities only marginally increases the DOS for this system. However, the full anharmonicity matrix (which mostly comprises negative values[20]) leads to a more significant increase. For the present naphthalene molecule, the excess in the natural logarithm of the density of states with respect to the harmonic reference is

approximately 1, which very nicely compares with the results obtained in Ref. 21 using a completely different semi-empirical model[9] and a tight-binding Hamiltonian.[22] The residual discrepancy between the two results is likely to originate from differences in the potential energy surfaces.

The accurate determination of quantum anharmonic DOSs is particularly useful for obtaining insight into the finite temperature properties of a molecular system. The vibrational contributions to the internal energy, heat capacity, and canonical entropy have been calculated by Laplace transformation from the microcanonical densities. The variations of the vibrational entropy with temperature are represented in Fig. 3 up to 1000 K for the three models of naphthalene.

For a more accurate estimation of anharmonic effects, the canonical entropies ΔS relative to the harmonic reference have also been calculated; they are shown in the inset of Fig. 3.

As expected from their similar DOSs, the two separable models yield comparable canonical entropies in the entire temperature range of 0–1000 K. Most anharmonic effects in naphthalene thus come from couplings. Looking more closely at the variations of ΔS with temperature, the diagonal anharmonicities are even seen to *lower* the entropy with respect to the harmonic value in the 250–750 K range. This is related to the presence of several positive coefficients among the χ_{ii}'s. Conversely, most couplings are negative and induce a concomitant increase in the entropy reaching
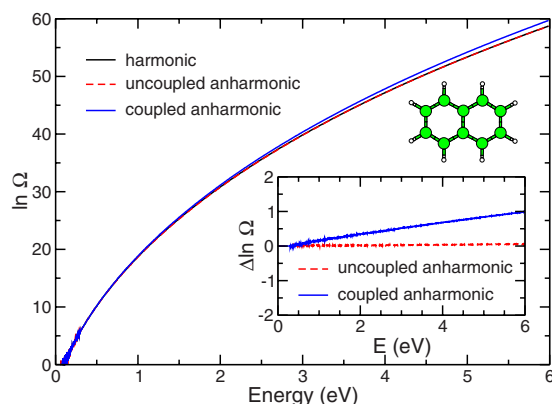

FIG. 2. (Color online) Density of vibrational states for the naphthalene molecule in the harmonic, separable anharmonic, and fully coupled anharmonic models as obtained using the WL method. The inset displays the difference in the natural logarithm of the densities for the two anharmonic models with respect to the harmonic reference.
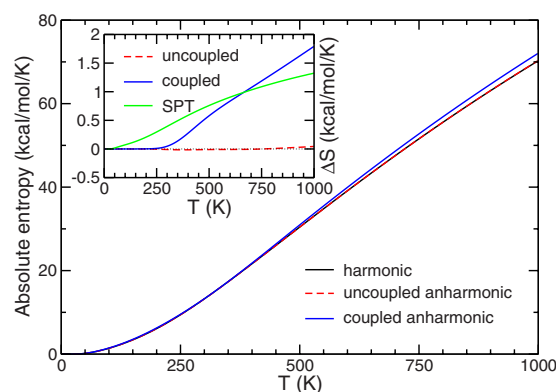

FIG. 3. (Color online) Absolute canonical entropy for the naphthalene molecule in the harmonic, separable anharmonic, and fully coupled anharmonic models obtained from the densities of states shown in Fig. 2 by Laplace transformation. The inset shows the entropies relative to their harmonic value in the two anharmonic models and the prediction of the SPT formula.

1.8 kcal/mol/K at 1000 K, a value within the accessible experimental range.

A convenient and inexpensive way of including anharmonicity and coupling effects on the thermal properties is the so-called simple perturbation theory (SPT) of Isaacson *et al.*,[23] in which the coupled system is treated as an effective harmonic system. The effective vibrational frequencies $\tilde{\nu}_i$ are obtained from the harmonic values ν_i and the anharmonic coefficients χ_{ij} as $\tilde{\nu}_i = \nu_i + 2\chi_{ii} + \Sigma_{j \neq i} \chi_{ij}/2$. The vibrational entropy for this effective harmonic model reads

$$S(T) = k_B \sum_i \left[\frac{\tilde{\nu}_i/k_B T}{e^{\tilde{\nu}_i/k_B T} - 1} - \ln(1 - e^{-\tilde{\nu}_i/k_B T}) \right], \quad (6)$$

where k_B is the Boltzmann constant. The results of the SPT approximation for the naphthalene molecule are shown in the inset of Fig. 3. As far as orders of magnitude are concerned, these results generally agree with our WL calculation. However, SPT overestimates the entropy below 700 K and underestimates it above this temperature. The present calculations provide a quantitative assessment of the accuracy of the perturbation approach.

Before concluding, a few remarks about the practical implementation of the WL sampling for coupled anharmonic models should be made. First, we have chosen here to use collective moves in the space of quantum numbers; however, the probability p of drawing ± 1 changes for each number should decrease with the number of degrees of freedom in order to keep the energy variations within reasonable limits. As in classical MC simulations,[24] we anticipate that moving a single quantum number should become more efficient for larger systems.

For a given coupled system, the parameters of the simulation (including the probability p and the possible need for dividing the energy range into multiple windows) should be determined by first considering the separable case. Comparison with the exact counting methods will then provide the appropriate parameters that can be subsequently transferred to the simulation for the coupled system. Once calculated, the quantum DOS can be used in multicanonical simulations of other properties at finite temperature.

Finally, although we have here only focused on vibrational degrees of freedom interacting through the second-order Dunham expansion, it is important to notice that the WL counting method is much more general. It could equally be applied to more complicated but explicit functions involving vibrations/rotations or Coriolis couplings.

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