

Low-energy unphysical saddle in polynomial molecular potentials

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Vibrational spectra of polyatomic molecules are often obtained from a polynomial expansion of the adiabatic potential around a minimum. For several molecules, we show that such an approximation displays an unphysical saddle point of comparatively small energy, leading to a region where the potential is negative and unbounded. This poses an upper limit for a reliable evaluation of vibrational levels. We argue that the presence of such saddle points is general.

1. Introduction

The morphology of the adiabatic potential energy surface (APES), especially its low-energy minima and saddle points, is at the basis of the quantum chemistry of reaction paths and conformational transitions [1]. The adiabatic potential governs the low-energy vibrational dynamics of a rigid molecule of N atoms and is a complicated function of $d = 3N - 6$ internal coordinates, such as bond lengths, bending or torsion angles ($d = 3N - 5$ for linear molecules). Its actual determination is usually a very demanding problem [2], as the information contents of a function of d coordinates grows exponentially with d . Global parametrizations of the APES computed with *ab initio* methods are presently accessible for small molecules [3–6]. A standard *local* parametrization, which was the main road to vibrational dynamics and is now mostly employed for medium-sized molecules [7], is provided by a Taylor expansion around the global minimum of the APES. For a deep minimum, one can isolate the vibrational contribution to the Hamiltonian, and expand it in normal modes [8]:

$$H = T + V = \frac{1}{2} \sum_a \hbar \omega_a (p_a^2 + q_a^2) + \frac{1}{3!} \sum_{abc} \phi_{abc} q_a q_b q_c + \frac{1}{4!} \sum_{abcd} \phi_{abcd} q_a q_b q_c q_d + \dots \quad (1)$$

q_a are the dimensionless normal-mode coordinates measured with respect to the equilibrium geometry and p_a are the conjugate momenta. The frequencies ω_a and higher-order constants $\phi_{ab\dots}$ of several molecules have been computed *ab initio* and sometimes refined by comparison with spectroscopic data [9]. For a simple molecule such as water, the anharmonic constants have been determined up to sixth order [10] and for several polyatomic molecules the literature reports calculations of third- and fourth-order constants [11–17]. It is widely recognized that the Taylor series should be used with caution, since it only converges within a limited radius [18]. The truncated series provides a locally accurate parametrization of the actual APES. Hereafter, we shall refer to the (finite) polynomial potential $V(q)$ in equation (1) as the PP.

We consider the available data for the PP of several molecules. In all cases we find a saddle point of comparatively small energy, leading to an unphysical dissociative region where the potential is not bounded from below. We also find that, for most molecules, the potential well accommodates very few quantum levels up to the saddle energy. To our surprise, this problem seems to be neglected: its analysis is the main purpose of the present study.

A main use of the polynomial expansion (1) is the calculation of a number of vibrational levels, usually by means of perturbation or variational theories, or by numerical diagonalization. Contrary to finite-order perturbative calculations, a non-perturbative determination of vibrational levels inevitably detects tunnelling

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to the unphysical region through the saddle. We show that sharp vibrational levels do occur only in the energy region below a quantum energy border, given by the sum of the energy of the lowest saddle (the classical border) plus the zero-point energy of the $d-1$ ‘transverse’ modes (of positive curvature) at the saddle point.

The paper is organized as follows: in section 2 we present the data for the lowest unphysical saddle point of several molecules, based on *ab initio* anharmonic constants available in the literature, and give arguments for the general occurrence of a low-energy saddle in polynomial approximations of the molecular APES. In section 3 we introduce the quantum energy border for the tunnelling regime, and illustrate its influence on the vibrational spectra of two molecules which respond very differently, water and ketene. We employ a non-perturbative method developed by us for evaluating the spectra, which is presented in the Appendix. In section 4 we discuss the results and the ensuing scenario.

2. The unphysical saddle

A unique feature of the polynomial expansion in equation (1) for the special case of diatomic molecules ($d = 1$) is that many even-power terms are *positive* (for example all even-power terms are positive for the Morse and Lennard-Jones functions). As a consequence, the truncation of the series to a positive even-power coefficient gives a lower-bounded potential, and thus a well-defined quantum problem, characterized by an infinite set of discrete levels. This feature of $d = 1$ is unfortunately lost when the power expansion (1) is extended to polyatomic molecules ($d > 1$): in all systems which we could obtain the anharmonic parameters for, we verified the occurrence of regions where the fourth-order PP is unbounded below.

Energy barriers separate different minima of a *physical* APES, corresponding to different local equilibrium configurations (isomers) of the molecule. The isomerization dynamics occurs mainly *via* quantum tunnelling or thermal activation through the lowest saddle of the barrier [19, 20]. Likewise, for the PP, energy barriers separate the region of the physical minimum around which the expansion is based and well grounded, from the *unphysical* regions where the potential drops to $-\infty$. The escape to the unphysical region is driven by the lowest saddle, which introduces an energy ‘border’ that limits the range for (metastable) quantum levels allowed in the physical well of the PP. Figure 1 illustrates this concept in a simple $d = 1$ -dimensional context, where we purposely

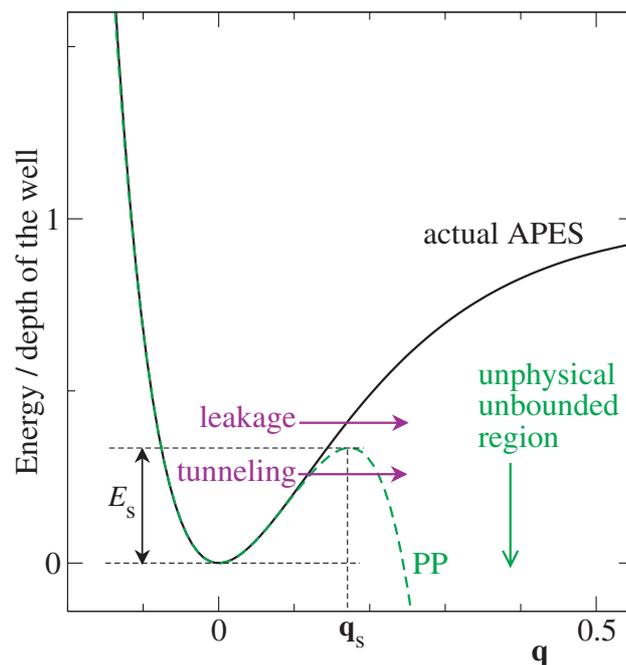


Figure 1. A typical 1-dimensional molecular potential (Morse, solid) and its 5th-order Taylor polynomial approximation (dashed) illustrating the presence of an unbounded region separated from the physical confining region by a barrier topping at a saddle point q_s .

truncated the polynomial expansion (1) to an odd order. It is clear that the saddle lies in a region where the polynomial has already become a poor approximation to the actual APES.

To determine the lowest saddle point of the PP of a polyatomic molecule, we first locate all stationary points in the neighbourhood of $\mathbf{q} = \mathbf{0}$. For this purpose, we compute analytically the gradient $\nabla_{\mathbf{q}}V$, and repeatedly solve the polynomial equation $\nabla_{\mathbf{q}}V = \mathbf{0}$ by the Newton method, starting from a scattered set of several thousand random initial points. This procedure generates a large number of stationary points of the PP. We then select the solution \mathbf{q}_s with the lowest positive energy E_s and check that it is indeed a saddle point, characterized by one negative and $d-1$ positive curvatures. Finally we verify that the PP, restricted to the straight line through the points $\mathbf{q} = \mathbf{0}$ and \mathbf{q}_s , has a shape qualitatively similar to the dashed line of figure 1, i.e. that tunnelling indeed occurs through a single barrier to a region where the potential drops to $-\infty$.

For several molecules, table 1 reports the height E_s of the lowest (unphysical) saddle point of the PP, measured from the bottom of the potential well. Surprisingly, these saddles are low: only about a few times a typical harmonic vibrational frequency of the molecule. As a result, few, if any, vibrational states sit

Table 1. Lowest saddle-point energy E_s , harmonic zero-point energy at the minimum $E_{zp}(0)$, harmonic transverse zero-point energy at the saddle point E_{zp}^\perp , of the 4th-order PP of several polyatomic molecules. For diatomics, the saddle energy E_s is replaced by the height of the maximum of the fifth-order Taylor expansion of a Morse potential fitting the experimental harmonic frequency and dissociation energy [21]. Energies are divided by hc and expressed in traditional spectroscopic wavenumber units cm^{-1} .

Molecular species	E_s/cm^{-1}	$E_{zp}(0)/\text{cm}^{-1}$	$E_{zp}^\perp/\text{cm}^{-1}$	Ref.
N_2	32834	1180	–	[21]
HCl	14919	1495	–	[21]
H_2O	6846	4717	4803	[10]
H_2O	7208	4712	4488	[11]
H_2S	8529	3335	3488	[11]
NO_2	13698	1890	1936	[11]
SO_2	6263	1537	1270	[11]
HOF	4624	3038	3043	[11]
HOCl	2821	2911	2893	[13]
$\text{H}_2\text{C}_2\text{O}$	834	6907	6641	[22]
C_2H_4	3483	11151	10815	[12]
CH_3OH	50	11398	11276	[23]

below E_s . The reported values of E_s of the diatomic molecules [21] set the characteristic scale given by the bond anharmonicities, in the 10^4cm^{-1} region. This can be regarded as an upper bound, as off-diagonal anharmonicities of the PP can only provide lower saddles, involving several normal coordinates at the same time. Indeed table 1 shows lower saddles for polyatomic molecules of increasing number of atoms. Especially low saddles are found for molecules characterized by soft torsional modes, such as methanol CH_3OH . The difference in energy between the two saddle heights obtained from different available PP of H_2O suggests an estimate of the accuracy of the reported values of E_s due to the approximations involved in *ab initio* calculations of the anharmonic parameters.

The occurrence of a saddle leading to an unphysical region is by no means specific of the PP of the molecules listed in table 1: we argue that this is a general feature to be found in the PP of most polyatomic molecules. Indeed, also for an even-power truncation, the PP can easily drop to $-\infty$ in some direction in \mathbf{q} space[†]. The precise value of the 4th-order parameters ϕ_{abcd} (including their sign) is determined by the *local*

properties of the physical APES at its minimum $\mathbf{q} = \mathbf{0}$, not by any requirement of confining behaviour at large distance: the PP of a real molecule easily contains negative semi-diagonal terms ϕ_{aabb} and sizable mixed terms ϕ_{abcd} , which in turn produce regions where the PP drops to $-\infty$. In practice, the same argument prevents confining behaviour also of 6th and higher even-order terms, and an even-power truncated PP does not behave any better, away from the physical minimum, than an odd-power truncated PP. Therefore, we consider it extremely unlikely (although technically possible) that a real polyatomic molecular potential may ever be found whose polynomial expansion at the minimum (truncated at any order > 2) is lower-bounded everywhere. Several methods to circumvent the incorrect behaviour of polynomial approximations at large q are commonly employed: for example, Morse coordinates for stretching modes are used to correct the unphysical power-law asymptotics of the PP [24–26].

3. The quantum energy border

As the PP has no lower bound, the associated Schrödinger problem is ill-defined. However, resonant states with complex energy values $E_a - i\Gamma_a$ usually exist in the well [19, 27–33]. Deep in the well, Γ_a is in general exponentially small and proportional to the Gamow factor $\exp(-2S/\hbar)$, where S is the imaginary-time action along the most probable tunnelling path inside the barrier. Resonances appear as sharp peaks in the spectral density, at energies E_a extremely close to the eigenenergies of the Schrödinger equation restricted to the well. As energy increases toward the threshold value, tunnelling evolves into a ‘leaking’ regime, characterized by the appearance of resonances whose imaginary part Γ_a is comparable to the real part [32], relics of further excited states in the well, strongly hybridized to the continuum.

In one dimension, the threshold coincides with the saddle energy E_s . For $d > 1$, an effect absent in the simple one-dimensional picture of figure 1 is to be considered: tunnelling through the barrier at the saddle point is hindered by the ‘transverse’ motion of the degrees of freedom perpendicular to the one crossing the barrier. These perpendicular degrees of freedom are associated with a minimum energy E_{zp}^\perp due to Heisenberg’s uncertainty, which adds to the saddle

[†]For example, the fourth-order terms $\phi_{1111}q_1^4 + \phi_{1222}q_1q_2^3 + \phi_{2222}q_2^4$ combine to $(\gamma^4\phi_{1111} + \gamma\phi_{1222} + \phi_{2222})q_2^4$ along the line $q_1 = \gamma q_2$, and the numeric coefficient $\gamma^4\phi_{1111} + \gamma\phi_{1222} + \phi_{2222}$ can easily be negative, provided that $|\phi_{1222}|$ is large enough and that γ is chosen suitably. Also, to make things worse, even though fully diagonal ϕ_{aaaa} terms are usually positive, there often occur semi-diagonal terms ϕ_{aabb} with negative sign.

height to determine the quantum energy border between the tunnelling and the leaking regimes

$$E_{\text{qb}} = E_s + E_{\text{zp}}^\perp. \quad (2)$$

As the study of tunnelling problems [23, 34] suggests, we approximate E_{zp}^\perp by its harmonic expression

$$E_{\text{zp}}^\perp \simeq \frac{1}{2} \sum_{i=2}^d \hbar \omega'_i \quad (3)$$

in terms of the $d-1$ real harmonic frequencies ω'_i at the saddle point (ω'_1 is the imaginary frequency associated with the tunnelling direction). Since, for most polyatomic molecules, E_{zp}^\perp is close to the zero-point energy of the ground state $E_{\text{zp}}(\mathbf{0})$ (see table 1), the raising of the energy border due to E_{zp}^\perp recovers a spectral range ($E_{\text{zp}}(\mathbf{0}) < E < E_{\text{qb}}$), where quasistationary vibrational levels are to be found, of extension comparable to the classical region for bounded motion ($0 \leq E \leq E_s$).

To illustrate the difficulties brought in by the unphysical saddle in polynomial approximations of APES, we compute non-perturbatively the vibrational spectra of two molecules, water and ketene, with different outcomes. For both, we employ *ab initio* quartic anharmonic potentials for the normal modes [10, 22]: while the PP of the water molecule features an energy range between the zero-point energy and the quantum border containing a number of vibrational levels, for ketene the range is so small to contain very few levels. We evaluate the levels $|E_a\rangle$ of the vibrational Hamiltonian H (1) by means of a non-perturbative technique equivalent to an exact diagonalization on a finite basis. Its advantage over standard Lanczos/Davidson diagonalization is a uniform precision throughout the whole spectrum. The Green function

$$G(E + i\varepsilon) = \langle \mathbf{v}_0 | (E + i\varepsilon - H)^{-1} | \mathbf{v}_0 \rangle \quad (4)$$

is computed with an iterative procedure on a set of values E . The initial state $|\mathbf{v}_0\rangle$ is chosen as an eigenstate of the harmonic part of H . The spectrum is obtained from the lineshape function

$$I(E) = -\frac{1}{\pi} \text{Im} G(E + i\varepsilon) = \frac{\varepsilon}{\pi} \sum_a \frac{|\langle E_a | \mathbf{v}_0 \rangle|^2}{(E - E_a)^2 + \varepsilon^2}. \quad (5)$$

Eigenvalues show up as peaks of $I(E)$, with heights proportional to the squared overlap of the exact eigenstates to the initial excitation. The parameter ε introduces a phenomenological Lorentzian broadening of the lines E_a .

A few words on the method for evaluating the Green function are necessary. First, one constructs a basis of harmonic states grouped into families T_i (tiers), $i = 0 \dots N$, adapted to the specific PP and the initial state $|\mathbf{v}_0\rangle$ [35–37]. Next, the Green function is evaluated through the exact recursive relation equation (A 3), as detailed in the Appendix. As the basis is finite, the spectrum consists of a finite number of real eigenvalues. By evaluating the spectra $I(E)$ with an increasing number of tiers N , one has a control of convergence in the regions below the quantum border, where tunnelling is suppressed. Above the border, no convergence is expected as the basis size is changed.

3.1. Water

We employ the *ab initio* quartic PP parameters listed in table 6 of [10]. The two real frequencies $\hbar\omega'_2 = 4758 \text{ cm}^{-1}$ and $\hbar\omega'_3 = 4849 \text{ cm}^{-1}$ at the lowest saddle point of H_2O ($E_s = 6846 \text{ cm}^{-1}$) are found to be so much larger than the three curvatures at the minimum, that $E_{\text{zp}}^\perp > E_{\text{zp}}(\mathbf{0})$ (table 1): this produces a rather narrow saddle, which pushes the quantum border up to $E_{\text{qb}} = 11\,649 \text{ cm}^{-1}$.

We take the harmonic fundamental excitation of the ω_1 (symmetric OH stretching) mode as initial state $|\mathbf{v}_0\rangle$ and obtain the spectrum in figure 2. The peaks, representing exact vibrational levels of the

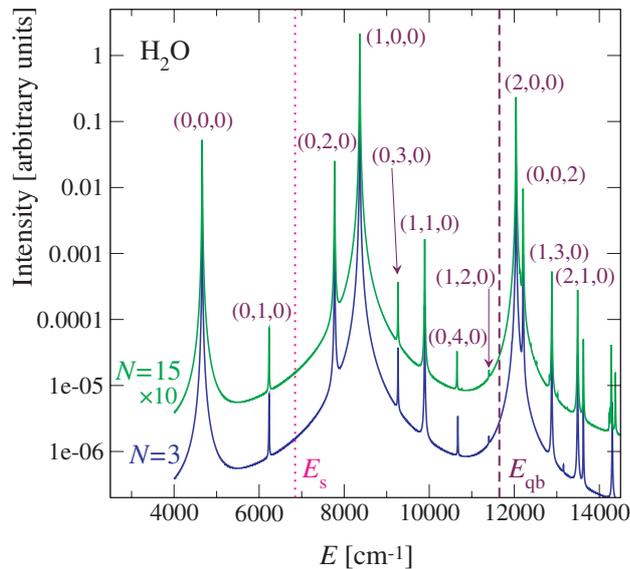


Figure 2. The spectrum of H_2O for initial excitation $|1,0,0\rangle$, computed with $N=3$ (294 states), and $N=15$ (16811 states), broadening $\varepsilon = 4 \text{ cm}^{-1}$. Below the quantum energy border, (dash line) convergence is satisfactory with relative error $\leq 1\%$. The main features seem to converge also above E_{qb} , but the appearance of new structures for larger N indicates non-negligible leakage.

PP, are assigned to the harmonic quantum numbers of the closest state resulting from standard second-order perturbation theory. Convergence is studied by increasing the tier number from $N = 3$ to $N = 15$. It is very good already using $N = 3$ tiers, thus showing the effectiveness of the tiers Green-function method. Hardly any tunnelling is observed below E_{qb} . Across E_{qb} , the appearance of the weak non-converging satellites confirms that the resonances in this region are affected by detectable leakage to the continuum. Indeed, since the lowest saddle lies in a direction involving mainly mode 1, the chosen initial state $|1, 0, 0\rangle$ promotes tunnelling. Nonetheless, the stability of several features even above E_{qb} indicates that a number of fairly long-lived physical states are so localized in the well that their overlap to the outside continuum is relatively small.

3.2. Ketene

As shown in table 1, according to the *ab initio* calculation of [22] the lowest saddle of the PP of ketene $\text{H}_2\text{C}_2\text{O}$ is very low. The resulting useful energy range is therefore extremely narrow, from $E_{zp}(\mathbf{0}) \simeq 6900 \text{ cm}^{-1}$ to $E_{qb} \simeq 7500 \text{ cm}^{-1}$. Only the ground state and the fundamental excitations of the lowest bending modes are located in the spectral region below the quantum border. The PP of ketene represents therefore a particular unfavourable case where no convergence is expected for any excitation.

Figure 3 shows the spectral region from the ground state to the CH stretching mode, obtained with the a_1 initial excitation $|1, 0, 0, 0, 0, 0, 0, 0\rangle$ of the CH symmetric stretching mode ν_1 , for different sizes of the basis. In this region, only a few fundamental and overtone/combination states of a_1 symmetry should be found. Instead, tens of spurious structures arise, which show no tendency to converge as the basis size increases. This is to be contrasted with the converging spectral range of H_2O , where a stable spectrum is achieved already with a small basis of $N = 3$ tiers.

4. Discussion

We show that polynomial approximations of molecular potentials usually display unphysical saddles that lead to regions where the potential is not lower bounded. The height of the saddle and the zero-point energy of transverse modes both determine a quantum energy border. Unless the saddle is very low, as e.g. in the PP of the ketene molecule, in the spectral region below the quantum border tunnelling is exponentially small and the standard perturbative

treatment of the anharmonic interactions usually provides a good approximation to the sharp level positions. Perturbative calculations are often extended to higher energies, based on the general belief that, like in the $d = 1$ Morse case, the second-order approximation compensates the wrong behaviour of the PP away from the minimum and reproduces the levels of a physical APES [38].

Our non-perturbative calculations show that, as energy is raised above the quantum border, resonances leave the tunnelling regime and couple more and more strongly to the continuum, practically washing out all spectral details. Such highly excited states are of scarce physical relevance anyway, since the extension of the associated wavefunction explores regions where the PP becomes a very poor approximation of the true APES.

The present results cast a shadow on the traditional use of the polynomial approximation of the physical APES for the calculation of highly excited vibrational or roto-vibrational spectra of polyatomic molecules. For example, in most molecules, IVR (intramolecular vibrational relaxation) spectra involve energy levels much above the saddle [39]. Hence, IVR applications of exact numerical methods, such as the Lanczos or Davidson algorithms [40–43] or the Green-function method proposed here, are bound to face the problem of the saddle of the PP. The consequent broadening

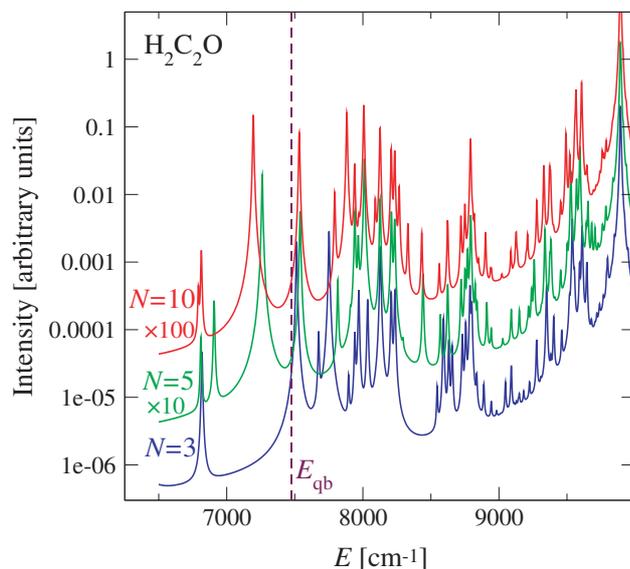


Figure 3. The spectrum of ketene for initial excitation $|1, 0, 0, 0, 0, 0, 0, 0\rangle$, computed with $N = 3$ (4299 states), $N = 5$ (8299 states), and $N = 10$ (18 299 states), broadening $\varepsilon = 4 \text{ cm}^{-1}$. No convergence is observed, even below the quantum energy border, due to sizable leakage. The relatively stable feature near $10\,000 \text{ cm}^{-1}$ corresponds to the energy position of the initial excitation.

of the resonant states poses an intrinsic limit to the spectral accuracy which can be obtained. Real progress may be achieved by the use of smarter local parametrizations of the APES (e.g. based on Morse coordinates [25, 26]).

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Appendix A: Non-perturbative evaluation of the Green function

We present a general procedure, inspired by [44] and indicated there as the ‘tiers method’, for the non-perturbative evaluation of the eigenvalues and spectral weights of a Hamiltonian decomposed as $H = H_0 + H'$. For definiteness, we consider the problem at hand: $H_0 = \sum \hbar\omega_b(a_b^\dagger a_b + 1/2)$ describes d independent oscillators, with eigenvectors $|\mathbf{v}\rangle = |v_1, v_2, \dots, v_d\rangle$, H' is the anharmonic part of the potential (1).

The first step of the method is to partition the unperturbed eigenvectors in families (tiers) T_0, T_1, \dots of decreasing perturbative relevance, such that the matrix representation of H is block-tridiagonal in the tiers. Symbolically we write the blocks as $H_{ii} = \langle T_i | H | T_i \rangle$ and $H_{i,i+1} = \langle T_i | H | T_{i+1} \rangle$. Depending on the problem under investigation, a set of unperturbed states $|\mathbf{v}_{0,\alpha}\rangle$ ($\alpha = 1, \dots, t_0$) is selected to form the initial tier T_0 . In the computations of this paper, T_0 contains a single initial state. The action of H' on T_0 gives new vectors: the basis states, which have non-zero overlap with them and are not in T_0 , are collected in T_1 . We label them as $|\mathbf{v}_{1,\alpha}\rangle$ ($\alpha = 1 \dots t_1$). For a finite set T_0 and an interaction H' which is a polynomial in the raising and lowering operators, tier T_1 and subsequent ones are finite. Next we consider the set $H'T_1$, and expand it in the eigenvectors already in T_0 and T_1 , plus new ones that are collected in tier T_2 . The process is iterated to produce further tiers T_3, T_4, \dots . Up to this point the method is simply a smart algorithm to generate systematically a good approximate basis for a quantum problem where some non-interacting part H_0 of the Hamiltonian can be singled out. Indeed, similar basis generation has been employed successfully in different contexts [41, 43–46]. However, the hierarchical basis structure and the corresponding block-tridiagonal form of the

Hamiltonian, suggest a natural iterative method to construct the spectrum.

The matrix element of the resolvent $\mathcal{G}(z) = (zI - H)^{-1}$ in T_0 is precisely the Green function in equation (4). We propose to compute it based on the following formula for the inversion of partitioned matrices, with square diagonal blocks (we omit unneeded terms):

$$M = \begin{pmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{pmatrix},$$

$$M^{-1} = \begin{pmatrix} [M_{11} - M_{12}(M_{22})^{-1}M_{21}]^{-1} & \dots \\ \dots & \dots \end{pmatrix}. \quad (\text{A } 1)$$

We apply this formula by identifying M with the matrix representations of $zI - H$ and M^{-1} with the resolvent $\mathcal{G}(z)$. The 4 blocks result from the separation of the basis into the set T_0 and the ordered set $T_1 \cup T_2 \cup \dots$. Off-diagonal matrix elements of M are due to H' only. Thus $M_{11} = zI_0 - H_{00}$ (I_0 is the unit matrix of size t_0 and $H_{00} = \langle T_0 | H | T_0 \rangle$). M_{22} is the matrix $(zI - H)$ expanded in the remaining tiers. $M_{12} = M'_{21}$ is a rectangular matrix of size $t_0 \times (t_1 + t_2 + \dots)$. By the tier construction, non-zero matrix elements of M_{12} are restricted to the leftmost submatrix of size $t_0 \times t_1$, that identifies with $-H'_{01} = -\langle T_0 | H' | T_1 \rangle$.

The aim of the calculation is to evaluate the block $(M^{-1})_{11} \equiv G(z) \equiv G^{(0)}(z) = \langle \mathbf{v}_0 | \mathcal{G}(z) | \mathbf{v}_0 \rangle$. The inversion formula (A 1) provides

$$G^{(0)}(z) = [zI_0 - H_{00} - H'_{01}G^{(1)}(z)H'_{10}]^{-1}, \quad (\text{A } 2)$$

where the $t_1 \times t_1$ matrix $G^{(1)}(z) = \langle T_1 | (M_{22})^{-1} | T_1 \rangle$. To evaluate it we use equation (A 1) again, with the blocks now resulting from the separation of the basis into the set T_1 and the set $T_2 \cup T_3 \cup \dots$. Now $M_{11} = (zI_1 - H_{11})$ and M_{22} is the matrix $(zI - H)$ expanded in the basis $T_2 \cup T_3 \cup \dots$. The matrix $G^{(1)}(z)$ coincides with the block $(M^{-1})_{11}$:

$$G^{(1)}(z) = [zI_1 - H_{11} - H'_{12}G^{(2)}(z)H'_{21}]^{-1},$$

where $G^{(2)}(z) = \langle T_2 | (M_{22})^{-1} | T_2 \rangle$. By iterating the same inversion formula (A 1) we obtain a chain of relations of the type

$$G^{(k-1)}(z) = [zI_{k-1} - H_{k-1,k-1} - H'_{k-1,k}G^{(k)}(z)H'_{k,k-1}]^{-1}. \quad (\text{A } 3)$$

In practice, the (in principle infinite) chain is truncated by approximately taking $G^{(N)}(z) \approx (zI_N - H_{NN})^{-1}$. This is the only approximation involved in this method and it amounts to neglecting the coupling of T_N to the subsequent tier. Starting from $G^{(N)}(z)$, one iterates

(A 3) back to the sought for matrix $G^{(0)}(z)$. This procedure is a matrix generalization of the continued fraction expansion for the inversion of tridiagonal matrices [47].

This method provides good evaluations of the position of the quasi-stationary states, including a rigorous treatment of all anharmonic resonances. These effects were mostly left out in the approximate treatment of [44], where off-diagonal terms M_{12} in equation (A 1) were neglected. The recursive calculation of the Green function (A 3) has several advantages with respect to the more traditional Lanczos method [41, 45, 48, 49]: (i) it provides equal accuracy through the whole spectrum, while the Lanczos method is more accurate close to the endpoints; (ii) it splits the Hilbert space into subspaces T_0, \dots, T_N to treat them one at a time; (iii) once the chain of matrices is set up, each frequency requires an independent calculation, which makes this method suitable for parallel calculations. Its main disadvantage is the rapid growth of the tier size t_i , for systems with many degrees of freedom. To fit the available CPU/memory limits, it is possible to cutoff the tier growth to some maximum size t_{\max} , as described in [45]. In general, the recursive method may become very costly in CPU time, since the evaluation of $G^{(0)}(E + i\varepsilon)$ requires N inversions for each sample frequency E , each inversion costing a time proportional to t_{\max}^3 . In the Lanczos method, a single chain of $N_{\text{Lanczos}} \approx 10^3$ iterations, each costing of the order of the Hilbert space size $\sim Nt_{\max}$, generates the whole spectrum.

The C++ code for computing the tier basis and the spectrum based on the Green-function recursive inversion formula (A 3) is available from [50].

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