LARGE AMPLITUDE GROUND STATE VIBRATIONAL COHERENCE INDUCED BY IMPULSIVE ABSORPTION IN CsI. A COMPUTER SIMULATION

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Computer simulations are presented to show that impulsive optical excitation of CsI, in various vibrational levels, can give rise to large-amplitude vibrational coherence in the ground electronic state. It is further demonstrated that using transient absorption spectroscopy, such motion may be directly detected, and that this scheme should be experimentally realizable using currently available laser sources. The quantum mechanical propagation method used in this study, proves to be well suited for the simulation of optical excitation of small molecules, under conditions where the assumptions of time-dependent perturbation theory are violated.

1. Introduction

Generation of intramolecular vibrational coherence, and its utilization in the study of molecular dynamics, is the subject of much recent activity. The growing interest in this area is to a large extent the result of the proliferation of subpicosecond laser systems that are capable of resolving intramolecular vibrational motions [1]. The ability to follow the evolution of molecular ensembles that are localized in controlled subvolumes of their energetically available vibrational phase space offers exciting prospects. In certain cases this may lead to time domain analogues of conventional frequency domain spectroscopies, essentially yielding the same information, but highlighting different aspects of the observable under study [2–4]. Photoinduced transitions from coherently prepared vibrational ensembles allows definition not only of the total internal energy, but also of the geometry and momenta of the nuclei. As demonstrated by computer simulation, addition of these variables to the list of controllable initial conditions in photolysis reactions may lead to new means of implementing mode-selective laser photochemistry [5].

Various spectroscopies have been employed to generate intramolecular vibrational motion in the ground and excited states. Impulsive Raman scattering (ISRS) has been used to create and detect the time evolution of optical phonons in molecular crystals, and of ground state intramolecular vibrations in pure organic liquids [6,7]. However, the Raman mechanism of field matter interaction afforded extremely small amplitudes of coherent motion. Ultrafast laser double-resonance techniques have demonstrated that large amplitude phase coherent nuclear motions, both bound and unbound, may be produced via impulsive absorption (IA) [8]. Terahertz oscillations in femtosecond absorption bleaching of various large dye molecules have been interpreted to be the result of intramolecular vibrational coherence both in the ground and excited states, induced by the combined action of resonant ISRS, and IA [9,10]. Despite the intense laser fields involved in these experiments, the modeling of these results has been conducted using time-dependent perturbation formalisms. This formalism is inadequate in cases where a significant portion of the population is radiatively transferred to the excited state, a situation that will result whenever the time–Rabi-frequency product is

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considerable. In principle this can be dealt with using perturbation theory, but the large number of terms required in the expansion make this approach impractical. In addition, whenever the force induced by the field is comparable to the internal forces, the dynamics of quantum propagation will be altered, due to field-induced alteration of the effective potential surfaces.

In order to take advantage of the full potential phase coherent molecular dynamics has to offer, reliable tools for the generation, detection, and interpretation of photoinduced nuclear coherent motion are required, including conditions that substantially alter the initial density matrix. For this purpose the induction of ground state vibrational coherence would be advantageous, since this state and excitations from it are usually the most reliably characterized. The generation of truly large amplitude vibrational coherences will involve both extremely intense fields and large optical conversions, which should violate the assumptions inherent to perturbation theories. It is therefore important that theoretical tools that are not subject to these limitations be used to model such experiments.

Time-dependent quantum mechanical integration techniques developed in recent years have been demonstrated to provide convenient means of modeling light–matter interaction under conditions that are not treatable by perturbative approaches [11]. Similar methods have recently been used to simulate the excited state dynamics of NaI vapour following impulsive promotion into upper electronic potentials, in an attempt to reproduce experimental results on this system [12]. In this communication we report the application of this approach to simulate the generation of large amplitude ground state vibrational coherence following impulsive optical excitation of vibrationally cold and selectively vibrationally excited CsI vapour. It is demonstrated that the structure of the potentials and the masses involved will make it possible to realize this scheme experimentally, with available laser sources [1,7,8]. These simulations show that transient absorption spectroscopy will be a facile method of detecting the time evolution of the coherent vibration. The method of calculation is especially attractive in that it does not separate the mechanisms of resonant Raman and optical absorption in the time development of the ensemble wavefunction.

The organization of the paper is as follows. In section 2 a brief description of the methods of calculation will be presented. Section 3 is dedicated to the presentation of simulation results along with a clear presentation of the approximations employed. These results will be discussed, and the feasibility of experimental realization will be assessed.

2. Method of calculation

The first step in modeling the dynamics of the CsI system, and its interaction with light, is establishing the degrees of freedom which are relevant to the experiment. Considering a light frequency of 3–4 eV, at least two electronic surfaces have to be considered. As for the nuclear motion, because of the large moment of inertia of CsI, and the low rotational temperature with which the molecule emerges from a molecular beam, the rotational motion can be ignored in this calculation. The calculation will therefore concentrate on the vibration motion on two electronic surfaces simultaneously. The potential for the calculation has been constructed from a Coulomb attraction and an exponential repulsion for the ground electronic surface, and a $C_6 r^{-6}$ attraction and an exponential repulsion in the excited electronic surface. Table 1 summarizes the potential parameters. The parameters chosen give a reasonable fit to the known spectroscopic measurements of this system.

The first step in the calculation has been to obtain the eigenstates of the ground potential surface. The relaxation method was used, which is based on propagating an initial guess for the ground state in imaginary time. Excited states are obtained by filtering out the previously calculated states and propagating in imaginary time until convergence is obtained. The Hamiltonian operator was represented on a grid. The Fourier method was used to calculate the kinetic energy operator [13]. The propagation in imaginary time was carried out by a Chebychev expansion of the evolution operator [14]. 17 eigenstates were calculated and stored for later use. Details of the calculation are summarized in table 1.

The next step was to calculate the absorption spec-

Table 1
Parameters of potential, grid, and propagation method, used in the simulation of CsI dynamics

Ground potential		Excited potential
$V_g = a\exp(-\beta r) - \frac{1}{r-r_{01}}$		$V_u = \exp[-d(r-r_e)] - \frac{C_6}{(r-r_{02})^6} + V_\infty$
$a = 131.569$ au		$d = 2.57102$ au
$\beta = 1.37042$ au		$r_e = 4.20$ au
$r_{01} = 0.893631$ au		$C_6 = 10.0$ au
$\mu = 0.3$ au		$r_{02} = 1.88972$ au
		$V_\infty = -0.002939921$ au
masses	$m_{Cs} = 132.909$ amu $m_I = 126.904$ amu	
grid	$N = 256$	$\Delta r = 0.008$
Chebyshev time propagation		$\Delta t = 11250$ au
time step for relaxation		$\Delta t = 1700$ au
time step for spectra		

trum for a weak excitation field obtained from different initial eigenstates of the ground surface. A new method to calculate this spectrum has been developed based on a Chebychev expansion [15] of the Green function. A similar scheme for the Raman spectrum was presented in ref. [16]. For weak excitation, the absorption spectra can be obtained by Fourier transforming in time of the dipole autocorrelation function,

$$a(\omega) = \int_{-\infty}^{\infty} \exp(-i\omega t)\langle\psi(0)|\mu|\psi(t)\rangle\,dt\,, \qquad (1)$$

where $\psi(0)$ is one of the ground state eigenfunctions, vertically moved to the excited surface. To propagate $\psi(0)$ in time the Chebychev formula is used,

$$\psi(t) \approx \exp[-i(\tfrac{1}{2}\Delta E + V_{min})t/\hbar] \times \sum_{n=0}^{N} a_n\left(\frac{\Delta E\,t}{2\hbar}\right)\Phi_n(-i\hat{H}_{norm})\psi(0)\,, \qquad (2)$$

where

$$\hat{H}_{norm} = 2\,\frac{\hat{H} - \hat{I}(\tfrac{1}{2}\Delta E + V_{min})}{\Delta E}\,,$$

ΔE is the energy range of the Hamiltonian operator, and Φ_n are the complex Chebychev polynomials. The expansion coefficients become: $a_n(\alpha) = 2J_n(\alpha)$, $a_0(\alpha) = J_0(\alpha)$ and $\alpha = \Delta E\,t/\hbar$. Considering the propagation algorithm, the use of eq. (2) requires the calculation of the operation of $\Phi_n(-i\hat{H}_{norm})$ on $\psi(0)$. This is calculated using the recursion relation of the Chebychev polynomials:

$$\phi_{n+1} = -2i\hat{H}_{norm}\phi_n + \phi_{n-1}\,, \qquad (3)$$

where $\phi_n = \Phi_n(-i\hat{H}_{norm})\psi(0)$. The recurrence is started by $\phi_0 = \psi(0)$ and $\phi_1 = -i\hat{H}_{norm}\psi(0)$. Inserting eq. (2) into eq. (1) and exploiting the symmetry with respect to time reversal of the Schrödinger equation one obtains the formula for the spectrum:

$$a(\omega) = \sum_{n=0}^{\infty} C_n\left(\frac{2\hbar(\omega-\omega_0)}{\Delta E}\right)\langle\psi(0)|\mu|\phi_n\rangle\,, \qquad (4)$$

where $\omega_0 = (\tfrac{1}{2}\Delta E + V_{min} + E_{shift})/\hbar$, where E_{shift} is the energy difference between the ground surface eigenstate $\psi(0)$ and the zero of the excited surface. C_n are basically the Fourier transforms of the Bessel functions a_n,

$$C_n(\beta) = 4(1-\beta^2)^{-1/2}\cos[n\arcsin(\beta)]$$

for n even ,

$$C_n(\beta) = 4(1-\beta^2)^{-1/2}\sin[n\arcsin(\beta)]$$

for n odd ,

and

$$C_0 = 2(1-\beta^2)^{-1/2}\,, \qquad (5)$$

where $\beta = 2\hbar(\omega-\omega_0)/\Delta E$. The actual number of terms N used in eq. (4) is determined by the spectral resolution $\Delta\omega > \Delta E/\hbar N$. The method is particularly efficient for photodissociation, because the resolution is determined naturally by the lifetime of the excited state τ leading to $N \approx \Delta E\,\tau/\hbar$. Fig. 1 displays the absorption spectrum of the ground $v=0$ and the excited $v=5$ states.

In order to calculate the absorption spectrum with intense laser fields the perturbative approach of eq. (1) has to be abandoned. The alternative is to solve the two surface dynamics using a semiclassical approximation for the electromagnetic field [5]. This leads to the coupled time-dependent Schrödinger equation:

$$i\hbar\frac{\partial}{\partial t}\begin{pmatrix}\psi_u\\ \psi_g\end{pmatrix}=\begin{pmatrix}\mathbf{H}_u & \mathbf{V}_{gu}\\ \mathbf{V}_{ug} & \mathbf{H}_g\end{pmatrix}\cdot\begin{pmatrix}\psi_u\\ \psi_g\end{pmatrix}, \qquad (6)$$

where ψ_u is the projection of the wavefunction on the upper surface. ψ_g is the projection of the wavefunction on the ground surface. $\mathbf{H}_i$ is the upper/lower surface Hamiltonian: $\mathbf{H}_i=\mathbf{T}_i+\mathbf{V}_i$ where $\mathbf{T}_i=\mathbf{P}^2/2m$ is the kinetic energy operator and $\mathbf{V}_i$ is the upper/lower potential energy surface. $\mathbf{V}_{ug}$ is the interaction potential, $V_{ug}=-\mu_{ug}E(t)$, where μ_{ug} is the dipole operator, and $E(t)$ represents the amplitude of a semiclassical electromagnetic field. The simulated experiment follows the evolution of the system subject to two Gaussian pulses with a time delay between them. The following form of the field has been chosen:

$$E(t)=A_0\exp[-(t-t_0)^2/2\sigma_0]\cos(\omega_1 t)$$
$$+A_1\exp[-(t-t_1)^2/2\sigma_1]\cos(\omega_2 t)\,, \qquad (7)$$

where t_i is the time of pulse i ($i=0, 1$), therefore $t=t_1-t_0$ is the time delay. σ_i is the pulse width, A_i is the pulse amplitude, and ω_i is the pulse's central frequency. The initial state of the propagation has been chosen to be one of the ground surface eigenfunctions. A short time propagation method has to be chosen because the Hamiltonian operator has explicit time dependence. The second-order differencing method [13] was selected because it treats naturally a multi-surface problem. The absorption can be followed either by the change in energy of the system after the pulse or the change in normalization of the wavefunction on the lower surface. Usually the first pulse was strong enough to prepare coherence and the second pulse was used as a probe with 10% of the amplitude of the first pulse.

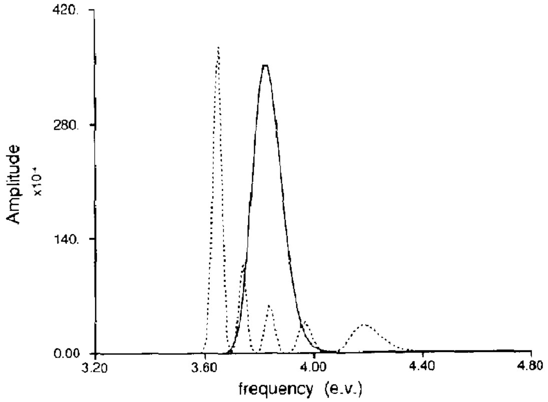

Fig. 1. Simulated absorption spectra of CsI vapour. For molecules uniformly in the zeroth vibrational level of the ground electronic state (solid line) and for molecules in the fifth vibrational level (dashed line). Spectra were calculated according to eq. (4); for details see text.

3. Results and discussion

Using the method described above, the time evolution of CsI vapour, during and after impulsive optical excitation with 60 fs pulses was simulated. This was carried out for populations initially in the zeroth, and in the fifth vibrational level in the ground electronic state. Calculation of a full thermal distribution of states was not carried out, which is needed to simulate an oven experiment. The effect of vibrational excitation is represented here by the $v=5$ simulations. In the two cases the frequency of excitation varied slightly to match the changes in the absorption spectra, and the pulse intensities were adjusted to provide nearly 50% excitation to the upper surface at the end of irradiation. The photon energies were 3.8 and 3.68 eV for the excitation of samples in $v=0$ and $v=5$, respectively. These frequencies were adjusted to be red-shifted with respect to the central frequency of the absorption. The results of calculation for the case of population initially in $v=5$ are depicted in fig. 2. A preferential coupling of molecules populating higher than average internuclear distances is observed during the process of ex-

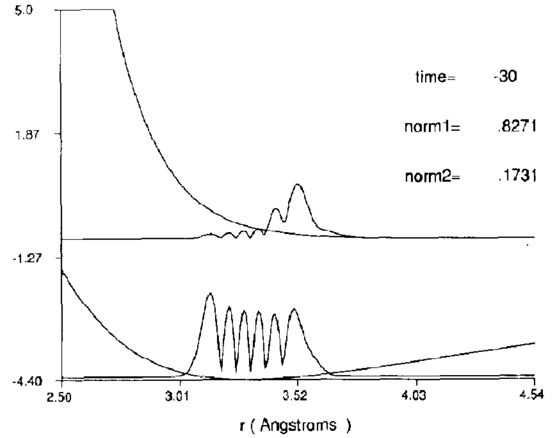

Fig. 2. Projections of the evolving wavefunction on the ground and excited states, during the initial stages of excitation of an ensemble uniformly in the fifth vibrational level of CsI. The displayed wavefunctions correspond to a time delay of 30 fs before the peak intensity of the excitation pulse. The potentials used for these calculations are also shown along with the instantaneous norms of the upper and lower projections of Ψ. The preferential excitation of population at larger than average internuclear distances is apparent in both simulations.

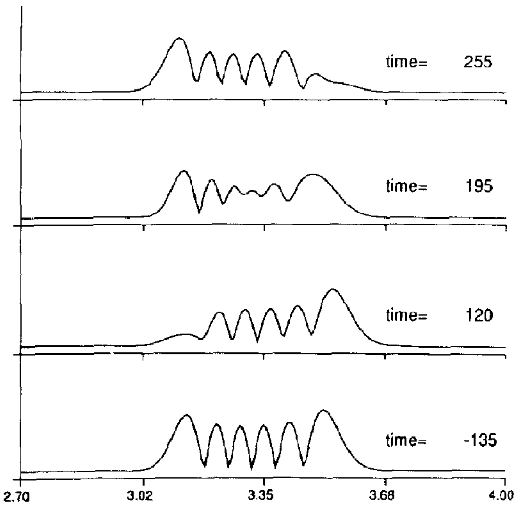

Fig. 3. Overlay of ground state vibrational wavefunctions at selected stages of evolution, after optical excitation of molecules in $v=5$, with a 60 fs laser pulse, centered at $t=0$. The delayed wavefunctions correspond to arrival at the classical turning points, with one point midway between these stages.

citation. The center of the Gaussian excitation pulse is at $t=0$, so the displayed wavefunctions correspond to times prior to the maximum of the excitation field. This is followed by periodic oscillations in $\langle r\rangle$, the average internuclear distance, which is a manifestation of the induced vibrational coherence. The population on the upper surface was absorbed when propagated beyond a certain r, so that no vibrational recurrences in the excited state were possible [8]. In any case the present propagation was continued for time spans that are shorter than the vibrational period in the excited state, excluding the importance of such recurrences on the conclusions of this study. The periodical time evolution is represented in fig. 3, which depicts an overlay of nuclear wavefunctions following excitation of molecules in $v=5$. The bottom is the initial state, followed by three wavefunctions which correspond with the classical turning points, and one intermediate point in the evolution.

The buildup of vibrational coherence requires the interference of multiple vibrational eigenstates. To demonstrate this in our case, the asymptotic wavefunctions were projected onto the eigenstate basis, providing the results plotted in fig. 4. The population remaining on the ground state following the excitation of the vibrationally cold sample has considerable population in the first four vibrational levels, resulting in an average quantum number $\langle v\rangle$ of 1.58, as depicted by the solid curve in fig. 4. In the case

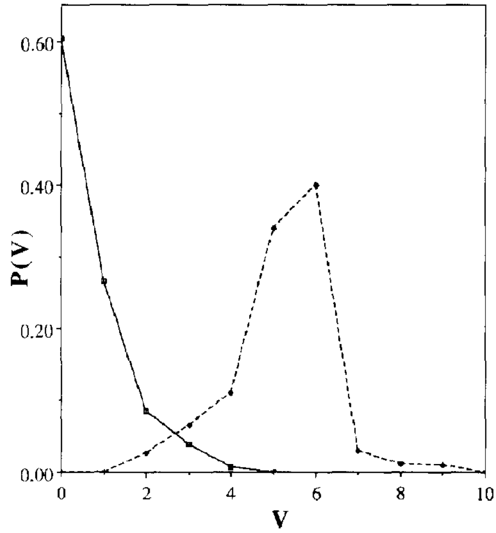

Fig. 4. Projections of the asymptotic ground state nuclear wavefunction after excitation, onto the vibrational eigenstates. The solid and dashed curves show the results for initial populations in $v=0$ and $v=5$ respectively.

of excitation of $v=5$, as shown by the dashed curve, the coherent superposition in the ground state is made up of vibrational levels above and below $v=5$ characterized by an average vibrational quantum level of 6.2. In these asymptotic states the periodic variations of $\langle r \rangle$ were calculated. In the case of excitation of the vibrationally cold sample this motion spans 0.14 Å, while excitation of a sample uniformly in the fifth vibrational level affords a quarter of an Å of coherent vibrational motion. *These results demonstrate that truly large-amplitude vibrational coherences, in the ground electronic state, are obtainable through this process.*

A facile method for experimental detection of these photoexcited vibrational coherent motions is transient absorption of the sample, using delayed ultrashort pulses which are of similar duration to the more intense excitation pulses. In order to simulate such experiments, time propagation calculations were run, where the sample was first excited with intense pulses as before, and at a variable delay subjected to another 60 fs pulse of one tenth the intensity. The delayed pulses were either at identical frequencies, or tuned to different frequencies. The results obtained for the transient absorption at a frequency identical to that of the excitation is depicted in the insert to fig. 5, for $v=0$ excitation. This plot represents the change in norm of the ground state population, due to the delayed pulses, as a function of the delay. Results are not presented for the first 300 fs, since the large amplitude of the excited state population above the ground state minimum gives rise to stimulated emission, and interpretation is difficult. After this population has propagated out sufficiently, the periodic variation of the probe pulse absorption is apparent.

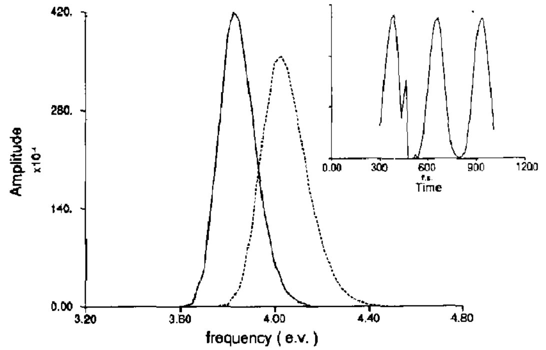

Fig. 5. Transient absorption spectra of CsI undergoing coherent vibrational motion, following impulsive optical excitation at $t=0$. Spectra are shown for time delays which correspond to extrema of this motion, for initial population in $v=0$. The insert shows transient absorbance of ultrashort probe pulses which are identical both in frequency and in duration to the excitation pulses, as a function of probe delay.

When the central frequency of the probing pulses is varied, the transient spectra of the vibrating ground state population may be probed. In this fashion the absorption spectra of populations, initially in the zeroth or the fifth vibrational levels has been simulated at times when the ensembles are close to their classical turning points, in this case at delays of 405 and 540 fs, respectively. The results are displayed in fig. 5 for the case of $v=0$ excitation. In this case the full spectral shift spans the width of the absorption prior to excitation. This agrees with the calculated fwhm of the $v=0$ level of ≈ 0.5 Å.

The question of experimental feasibility of the proposed scheme may be addressed directly. Obtaining tunable 60 fs pulses has been demonstrated by various groups, and should not pose a problem [17]. The intensity required for conducting these experiments may be calculated either directly from the cross sections for absorption, or using the calculated Rabi frequency. The integrated absorption band yields the value of ≈ 2 D for μ_{ug}. Since almost complete inversion of population resonant with the field is affected, we demand that the Rabi-frequency–time product fulfill the following relation, $V_{\mathrm{ug}}\sigma_i/\hbar=\pi$. Implicit is the approximation of square pulses. This leads to A_0 of $\approx 8\times10^8$ V/M, or $\approx 10^{11}$ W/cm^2. The required intensity may also be estimated using the absorption cross section, which is roughly a few times 10^{-17} cm^2. Assuming 50% absorption and 60 fs pulses leads to a similar order of magnitude for the intensity. No more than a rough estimate could be derived, since literature information is for absorption from broad thermal distributions of hot vapours. Such peak powers are routine in femtosecond experiments, and can even be propagated through condensed materials. This intensity is sufficient to invalidate a perturbative approach, due to the extremely large oscillator strength of this transition. Since the interaction Hamiltonian contains the dipole-moment–field-vector product, all arguments concerning power, involving resonant interactions, will scale with the magnitude of the transition dipole. This also explains the convenience of femtosecond work on alkali halides.

One of the most attractive features of the method of calculation used in this study is the straightforward way in which it deals with all linear and nonlinear interactions of the material system with the field. To a certain degree the variety of processes participating in the development of the system studied here has been artificially limited by disregarding the existence of higher excited states. This may be significant when intense fields such as those proposed here are employed. However, even at this level of simplification, these virtues can be readily appreciated. This is apparent when comparing with perturbative calculations of similar phenomena [9]. While the authors of this paper have correctly pointed out the importance of simultaneous consideration of both IA and resonant ISRS in absorbing Raman-active media, their method of calculation necessarily segregates these effects into separate Feynman diagrams, leading after considerable mathematical effort, to results limited to the small signal regime. It is worthwhile pointing out that in its present form the quantum propagation theory is not set up to simply include phase and population relaxation phenomena which are included in these perturbative calculations. Work aimed at casting it in a form that will enable this is under way [18].

4. Conclusions

We have demonstrated through computer simulations that impulsive optical excitations of alkali halide molecules may give rise to large amplitude ground state coherent vibrational motions, using experimentally available ultrashort laser pulses. We have concentrated on CsI due to the low ground state vibrational frequency in this molecule. However, sufficiently short laser pulses should allow experimentation with lighter analogs. We have also shown that femtosecond transient absorption spectroscopy is a facile experimental method for detecting such motions. The quantum mechanical technique with which the molecular dynamics were simultaneously simulated, on both the ground and excited surfaces, has proven to be convenient and well adapted for predicing the evolution of small molecules under the influence of very strong fields, in situations where the assumptions of perturbation theories are violated. These methods can be extended to include more degrees of freedom, either classically or quantum mechanically.

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