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Full-dimensional simulation of alignment dynamics of H_2He^+ in laser fields

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Introduction. The investigation of the spatial alignment and orientation of molecules by laser fields is an active research area with potential applications in reaction control, isotope and photofragment separation, and molecule trapping.[1] The theoretical simulation of the alignment dynamics of polyatomic molecules is most commonly carried out in a rigid rotor approximation, although perturbative corrections and reduced dimensional variational approaches have also been investigated.[2,3] It is known from spectroscopic studies[4] that in the case of floppy molecules exhibiting large amplitude, anharmonic vibrations and strong rovibrational couplings, the rigid rotor approximation and its perturbative extensions cannot provide accurate descriptions. For such molecules, non-perturbative, variational approaches are required for the simulation of their rovibrational motion and alignment dynamics.

In the present study, we propose a theoretical framework, with which it becomes possible to simulate the alignment dynamics of non-rigid polyatomic molecules by taking into account their vibrational motion and rovibrational couplings. As an illustrative example, the alignment dynamics of the weakly bound H_2He^+ complex is demonstrated. The rovibrational motion induced by an external laser pulse is described by full-dimensional variational computations.

Theory of field-matter interaction. In order to simulate spatial alignment dynamics, one needs to solve the time-dependent Schrödinger equation

$$i\hbar\frac{\partial|\Psi\rangle}{\partial t} = \hat{H}(t)|\Psi\rangle, \qquad \hat{H}(t) = \hat{H}_0 - \boldsymbol{\varepsilon}(t)\boldsymbol{\mu} - \frac{1}{2}\boldsymbol{\varepsilon}(t)\big(\boldsymbol{\alpha}\boldsymbol{\varepsilon}(t)\big) \qquad (1)$$

where $\hat{H}_0$, $-\boldsymbol{\varepsilon}(t)\boldsymbol{\mu}$ and $-(1/2)\,\boldsymbol{\varepsilon}(t)\big(\boldsymbol{\alpha}\boldsymbol{\varepsilon}(t)\big)$ are the field-free rovibrational Hamiltonian, the permanent dipole interaction with the external field $\boldsymbol{\varepsilon}(t)$, and the induced dipole interaction with the external field $\boldsymbol{\varepsilon}(t)$, respectively. Our approach to deal with the computational task of solving Eq. (1) is composed of two steps as summarized in Figure 1.

The first step uses variants of efficient nuclear motion computer codes to determine bound rovibrational states $|\Psi_n\rangle$, satisfying the time-independent nuclear Schrödinger equation $\hat{H}_0|\Psi_n\rangle = E_n|\Psi_n\rangle$, leading to a small set of basis functions capable of describing the rovibrational motion of the system. In the second step, the $|\Psi_n\rangle$ functions are used to expand the time-dependent rovibrational wavepacket $|\Psi\rangle$, leading to a compact matrix representation of the Hamiltonian, with which time-propagation can be carried out in a straightforward manner. Based on the properties of the field-free states, the time evolution of physical quantities induced by the laser field can easily be monitored.
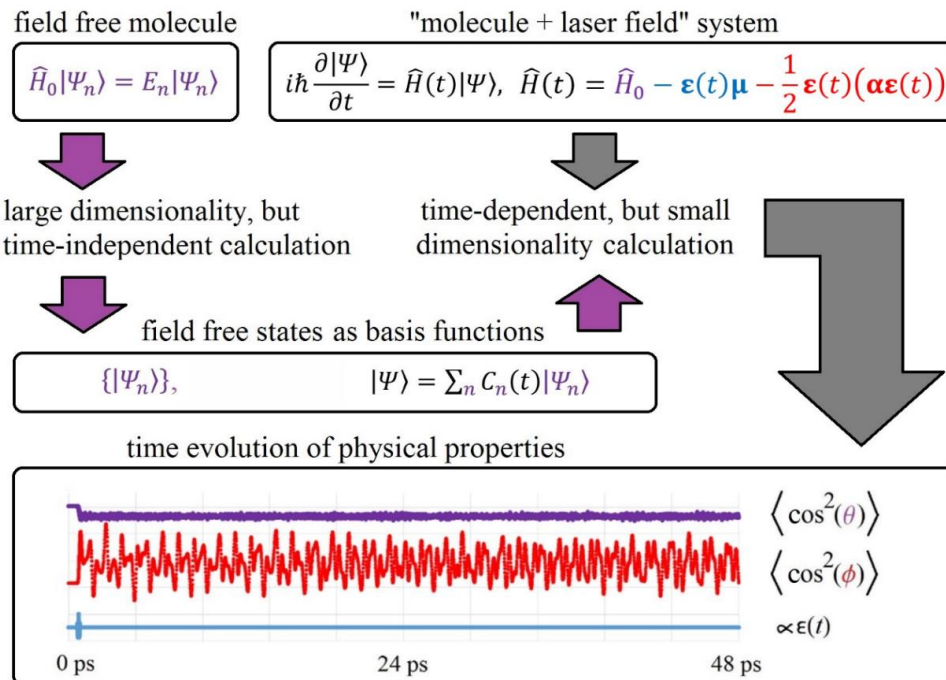
Figure 1. Pictorial representation of the theoretical framework to investigate laser-induced alignment dynamics of polyatomic molecules. See text for the meaning of $\widehat{H}_0$, E_n, $|\Psi_n\rangle$, $\boldsymbol{\mu}$, $\boldsymbol{\alpha}$, $\boldsymbol{\varepsilon}(t)$, and $|\Psi\rangle$. ϕ is the angle of spatial alignment and θ represents an internal degree of freedom.

Alignment dynamics of H_2He^+. Based on the theoretical approach presented above, the alignment dynamics of H_2He^+ was simulated for several different laser conditions. It was found that when H_2He^+ is exposed to a long, 4 ps halfwidth laser pulse ($\lambda = 800$ nm, $I = 10^{13}$ Wcm^{-2}) the molecule undergoes adiabatic alignment. If a much shorter laser pulse is used (halfwidth = 200 fs, $I = 2\times10^{13}$ Wcm^{-2}), a rotational wave packet is created, which shows field-free (diabatic) alignment dynamics with a full revival time of around 4 ps. Finally, by changing the wavelength of the laser closer to resonance with the first vibrational excitation energy ($\lambda = 25000$ nm, $I = 10^{12}$ Wcm^{-2}, halfwidth = 150 fs), H_2He^+ undergoes significant structural changes, with the structural parameters showing rapid fluctuations in time. This leads to time-dependent rotational constants, thus very complicated alignment dynamics with no evident revival time.

[1] See for example: H. Stapefeldt and T. Seideman, Rev. Mod. Phys. **75**, 543 (2003); Y. Ohshima and H. Hasegawa, Int. Rev. Phys. Chem. **29**, 619 (2010); M. Lemeshko, R. V. Krems, J. M. Doyle and S. Kais, Mol. Phys. **111**, 1648 (2013).

[2] E. Hamilton *et al.*, Phys. Rev. A **72**, 043402, (2005).

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[4] P. R. Bunker and P. Jensen, Molecular Symmetry and Spectroscopy, NRC Research Press, Ottawa, (1998).