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Accessing electronic correlations by half-cycle pulses and time-resolved spectroscopy

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Ultrashort nonresonant electromagnetic pulses applied to effective one-electron systems may operate on the electronic state as a position or momentum translation operator. As derived here, extension to many-body correlated systems exposes qualitatively new aspects. For instance, to the lowest order in the electric field intensity the action of the pulse is expressible in terms of the two-body reduced density matrix enabling us to probe various facets of electronic correlations. As an experimental realization we propose a pump-probe scheme in which after a weak, swift "kick" by the nonresonant pulse the survival probability for remaining in the initial state is measured. This probability we correlate to the two-body reduced density matrix. Since the strength of electronic correlation is bond-length sensitive, measuring the survival probability may allow for a direct insight into the bond-dependent two-body correlation in the ground state. As an illustration, full numerical calculations for two molecular systems are provided and different measures of electronic correlations are analyzed.

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I. INTRODUCTION

Recent experiments demonstrated the feasibility of ultrashort attosecond laser pulses and their use in combination with other optical pump-probe techniques to access various facets of the electronic and ionic dynamics [1–5]. Of a special relevance here are strongly time-asymmetric pulses. The simplest example is a mono cycle, time asymmetric pulse for which one half-cycle could be short and strong and the other half-cycle could be longer but weaker in a way that the time integral over the electric field amplitude vanishes, as required for a propagating pulse. When interacting with matter, the effect of two half-cycles could be quite different [6–9]. For instance, if the first half-cycle (with duration τ) is shorter than the time of relevant transitions taking place in the system, while the second, weaker half-cycle is much longer, then the effect of the whole pulse is mainly governed by the first half-cycle of the pulse (HCP). Henceforth we refer to this situation as the HCP case. The second half-cycle may act as an off-set dc tail (if weak or long enough).

In this limit it is convenient and sometime sufficient to introduce theoretically the notion of HCP kick as a useful idealization of the action of the whole pulse [6,10–21]: Namely, in the HCP case, the system is insensitive to the details of the pulse temporal shape. This allows relating the action of HCP to that of a kick, i.e., a δ function in time. Substantial simplifications of the triggered quantum dynamics then follow. We will demonstrate below that by performing measurements in an appropriate setup on the system immediately after such an excitation allows us to infer the strength of the electronic correlation in the system and its dependency on the internal structure, and to quantify the entanglement. The experimental arrangement that we suggest is the following: We start from the ground state, of say some molecular structure (another stationary case is also possible), and "shake" the electronic system by a weak but short HCP. As the system evolves and possibly dissociates we measure, e.g., via the time-resolved photoemission [22], the initial-state remaining, i.e., what we will call the *survival probability*. Detecting only the kinetic energies of the dissociating ions upon the kick, one may access information on the ionic time evolution that can be used when measuring the time-resolved survival probability as a function of the molecular bond (since at this particular time one has information on the molecular bond distance). Currently we are not aware of any corresponding experiment to this proposal, however, the ingredients of the suggested setup, such as HCP, time-resolved photoemission were demonstrated [23–25]. From the survival probability we deduce features akin to the reduced two-particle density matrix.

Specifically, the envisaged experiment should measure upon the kick the initial state occupation probability as a function of the evolving internuclear distance. It is this quantity which we calculated numerically and will be discussing below. Knowing (from theory or experiment [26,27]) the molecular bond distance upon the nonresonant pulse excitation we can so image the time evolution of the survival probability. We relate it below to the reduced two-particle density matrix which vanishes for the single determinantal states and, thus, can be used as a measure of electronic correlations.

So the key point of this study is how to measure and quantify electronic correlations. In Sec. II we give an explicit expression for the probability of the system to remain in its ground state after the application of a δ-like pulse. While for one-electron systems the quantum dynamics was discussed by many authors the nontrivial part tackled here is the many-body nature of the problem. In Sec. III we put the discussed probability in the context of other proposed measures of electronic correlations: the Frobenius norm of the second *cumulant matrix* and the *von Neumann entropy*. Stretching molecular bonds incur in general a change in the amount of correlations in the electronic subsystem. The proposed experiment is illustrated by numerical simulations which show what a possible outcome might be expected (Sec. IV). The dependence of different correlation measures on the interatomic distances is studied, and analytical expressions in the asymptotic regime are obtained. Additionally, our calculations allow us to test numerically for important inequalities for the entropy measures.

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II. THEORY

Consider an N-electron system in its ground state. Its electronic properties are completely described by the many-body wave function $\psi_0(1,2,\ldots,N)$. Although the choice of the gauge is irrelevant for the present discussion we will assume here the light-matter interaction to be given in the length gauge by the dipole operators $\hat{d}^\alpha$, where α denotes a projection (determined by the pulse polarization). The coupling operators are of one-particle type, Hermitian $[\hat{d}^\alpha = (\hat{d}^\alpha)^\dagger]$ and of vector character. By choosing a suitable one-particle basis we can cast the light-matter interaction in the second-quantized form $\delta H(t) = -\sum_\alpha \sum_{i,j} d^\alpha_{ij} E^\alpha(t)\hat{c}^\dagger_i \hat{c}_j$, where E^α are the components of the electric field vector. Acting on the system with a pulse that has the time-dependence $E^\alpha(t) = E^\alpha_0 \delta_\epsilon(t)$ with a peak amplitude at $t=0$, we can write the state of the system at $t=\epsilon$ shortly after the pulse as

$$\psi_+ = e^{i\sum_{i,j} S_{ij}\hat{c}^\dagger_i \hat{c}_j}\psi_0 = e^{i\hat{S}}\psi_0. \tag{1}$$

δ_ϵ is a regularized version of the mathematical δ distribution on $[0,\epsilon]$ interval and $S_{ij} = -\int_0^\epsilon dt \sum_\alpha d^\alpha_{ij} E^\alpha_0 \delta_\epsilon(t)$ has a dimension of an action (we use atomic units throughout the text). Mapping the pulse generated state on the ground (initial) state ψ_0, i.e., taking the overlap $\langle\psi_0|\psi_+\rangle$ of (1), we obtain the survival (recurrence) probability to be in ψ_0 after the pulse. This quantity is central to the following discussion.

The *quantum-mechanical* average of the operator $\hat{S} = \sum_{i,j} S_{ij}\hat{c}^\dagger_i \hat{c}_j$ can be treated like any statistical average using the *cumulant expansion*:

$$\langle\psi_0|\psi_+\rangle = \exp\left\{\frac{i}{1!}\mathfrak{S}_1 + \frac{i^2}{2!}\mathfrak{S}_2 + \frac{i^3}{3!}\mathfrak{S}_3 + \cdots\right\}. \tag{2}$$

The correlation functions are well known:

$$\mathfrak{S}_1 = \langle\hat{S}\rangle, \quad \mathfrak{S}_2 = \langle\hat{S}^2\rangle - \langle\hat{S}\rangle^2, \tag{3a}$$

$$\mathfrak{S}_3 = \langle\hat{S}^3\rangle - 3\langle\hat{S}^2\rangle\langle\hat{S}\rangle + 2\langle\hat{S}\rangle^3. \tag{3b}$$

These averages can be computed in terms of reduced density matrices (RDM)

$${}^1D^i_j = \langle\psi_0|\hat{c}^\dagger_i \hat{c}_j|\psi_0\rangle, \tag{4a}$$

$${}^2D^{ik}_{jl} = \langle\psi_0|\hat{c}^\dagger_i \hat{c}^\dagger_k \hat{c}_l \hat{c}_j|\psi_0\rangle, \tag{4b}$$

$${}^3D^{ikm}_{jln} = \langle\psi_0|\hat{c}^\dagger_i \hat{c}^\dagger_k \hat{c}^\dagger_m \hat{c}_n \hat{c}_l \hat{c}_j|\psi_0\rangle. \tag{4c}$$

In order to do so we need some additional notations for operators. $\hat{S}^n$ is a n-body operator, i.e., it is given by an expression containing n creation and n annihilation operators. Let $[\hat{S}^n]$ denote a one-particle operator which is given by the nth power of $\hat{S}$ operator in the first quantization, i.e.,

$$[\hat{S}^n] = \sum_{ij}(S^n)_{ij}\hat{c}^\dagger_i \hat{c}_j.$$

In these notations:

$$\begin{aligned}\mathfrak{S}_2 &= -\langle\hat{S}\otimes\hat{S}\rangle + \langle[\hat{S}^2]\rangle - \langle[\hat{S}]\rangle^2,\\ \mathfrak{S}_3 &= -\langle\hat{S}\otimes\hat{S}\otimes\hat{S}\rangle - 3\langle[\hat{S}^2]\otimes\hat{S}\rangle + \langle[\hat{S}^3]\rangle\\ &\quad + 3\langle\hat{S}\otimes\hat{S}\rangle\langle\hat{S}\rangle - 3\langle[\hat{S}^2]\rangle\langle[\hat{S}]\rangle + 5\langle[\hat{S}]\rangle^3,\end{aligned}$$

where the ${}^p\hat{A}\otimes{}^q\hat{B}$ denotes the *normal form* of the product ${}^p\hat{A}$ and ${}^q\hat{B}$, the p- and q-body operators, respectively. It is defined as follows:

$$\begin{aligned}{}^p\hat{A} &= \sum_{\mathbf{i},\mathbf{j}} A^{\mathbf{i}}_{\mathbf{j}}\hat{c}^\dagger_{i_1}\cdots\hat{c}^\dagger_{i_p}\left(\hat{c}_{j_1}\cdots\hat{c}_{j_p}\right)^T,\\ {}^q\hat{B} &= \sum_{\mathbf{k},\mathbf{l}} B^{\mathbf{k}}_{\mathbf{l}}\hat{c}^\dagger_{k_1}\cdots\hat{c}^\dagger_{k_q}\left(\hat{c}_{l_1}\cdots\hat{c}_{l_q}\right)^T,\\ {}^p\hat{A}\otimes{}^q\hat{B} &= \sum_{\mathbf{i},\mathbf{j}}\sum_{\mathbf{k},\mathbf{l}} A^{\mathbf{i}}_{\mathbf{j}}B^{\mathbf{k}}_{\mathbf{l}}\hat{c}^\dagger_{i_1}\cdots\hat{c}^\dagger_{i_p}\hat{c}^\dagger_{k_1}\cdots\hat{c}^\dagger_{k_q}\\ &\quad\times\left(\hat{c}_{l_1}\cdots\hat{c}_{l_q}\hat{c}_{j_1}\cdots\hat{c}_{j_p}\right)^T.\end{aligned}$$

In these expressions **i**, **j** and **k**, **l** are the p- and q-dimensional vectors of indices.

For our discussion it is instructive to introduce the *cumulant density matrices* [28,29] ${}^p\Delta$ which allow us to decompose the p-RDM in terms of correlated (connected) p-particle correlator and products of lower order correlators [30]:

$$\frac{1}{1!}{}^1D^i_j = {}^1\Delta^i_j, \tag{5a}$$

$$\frac{1}{2!}{}^2D^{ik}_{jl} = {}^1\Delta^i_j \wedge {}^1\Delta^k_l + {}^2\Delta^{ik}_{jl}, \tag{5b}$$

$$\frac{1}{3!}{}^3D^{ikm}_{jln} = {}^1D^i_j \wedge {}^1D^k_l \wedge {}^1D^m_n + 3\,{}^2\Delta^{ik}_{jl}\wedge{}^1D^m_n + {}^3\Delta^{ikm}_{jln}, \tag{5c}$$

where $\wedge$ denotes the *wedge product* [31] (for mathematical details we refer to a treatise on differential forms [32] where $\wedge$ appears under the name exterior product). We have, for instance,

$${}^1\Delta^i_j \wedge {}^1\Delta^k_l = \tfrac{1}{2}\left({}^1\Delta^i_j\,{}^1\Delta^k_l - {}^1\Delta^i_l\,{}^1\Delta^k_j\right).$$

The $1/n!$ prefactor on the right-hand side of Eqs. (5) appears naturally when the density matrices are written in the first quantization:

$$\begin{aligned}&\frac{1}{n!}{}^nD(1,\ldots,n;1',\ldots,n')\\ &\quad= \int \psi^*_0(1,\ldots,n,n+1,\ldots,N)\\ &\qquad\times\psi_0(1',\ldots,n',n+1,\ldots,N)d(n+1,\ldots,N),\end{aligned} \tag{6}$$

where $i \equiv (r_i,s_i)$ denotes a collection of space and spin coordinates.

Returning back to Eq. (2) we find by direct comparison $\frac{1}{1!}\mathfrak{S}_1 = \sum_{ij} S_{ij}{}^1D^i_j$. It is, however, the second cumulant that gives the lowest order (in $|\mathbf{E}_0|^2$) contribution to the survival probability, namely

$$\begin{aligned}|\langle\psi_0|\psi_+\rangle|^2 &\approx \exp[-\mathfrak{S}_2] \approx 1 - \mathfrak{S}_2,\\ \mathfrak{S}_2 &= \sum_{ijkl} S_{ij}S_{kl}{}^2D^{ik}_{jl} + \sigma^2_S.\end{aligned} \tag{7}$$

Thus, $\mathfrak{S}_2$ can be written as the averaged value of a two-body operator [first term in Eq. (7)], whereas $\sigma^2_S = \langle[\hat{S}^2]\rangle - \langle[\hat{S}]\rangle^2$ is computed from 1-RDM. This equation can be written in an alternative form. Consider the natural orbital basis (i.e., a basis in which 1-RDM is diagonal):

$$
\begin{aligned}
\mathfrak{S}_2 &= \sum_{ijkl} S_{ij} S_{kl} \left[{}^2\Delta^{ik}_{jl} + f_i f_k (\delta_{ij}\delta_{kl} - \delta_{il}\delta_{kj}) \right] \\
&\quad + \sum_{im} (S_{im} S_{mi} f_i - S_{ii} S_{mm} f_i f_m) \\
&= \sum_{ijkl} S_{ij} S_{kl} {}^2\Delta^{ik}_{jl} + \sum_{im} |S_{im}|^2 f_i (1 - f_m), \qquad (8)
\end{aligned}
$$

where f_i is the occupation number of the ith natural orbital. Despite the fact that the second term in Eq. (8) has a form of the *Fermi golden rule* [33] the latter is only valid for sufficiently long pulses (adiabatic switching).

Equation (7) is a quite remarkable result as it allows us to express the averaged 2-RDM in terms of experimentally measurable quantities: the survival probability and the mean square deviation of an excitation operator. Alternatively, one can use the form (8) to access the ${}^2\Delta$ cumulant as a correction to the single-particle result. A possible experiment that we sketched in the Introduction could be a pump-probe setup in which the system is excited nonresonantly by a half-cycle pump pulse and the probe laser pulse is used to monitor the ground state occupation. We envisage an application to molecular systems in which the amount of electronic correlations and, thus, $\langle[\hat S \otimes \hat S]\rangle$ are driven by changes of geometry. On the other hand, the one-body part σ_S^2 is a quantity that is weakly dependent on the geometric configuration (see also the discussion below) and can also be easily computed [34].

For a faithful correlation measure it is desirable to minimize the artifacts coming from the dependence of $\hat S$ on the system's geometry. Consider a system subject to stretching. The values of the matrix elements S_{ij} can be quite large as compared to the equilibrium geometry. Correspondingly, the value of $\mathfrak{S}_2$ obtained according to Eqs. (7) and (8) will be at variance with the equilibrium value—the effect that is not necessarily reflecting properties of ${}^2\Delta$. It is possible, however, to suppress to some extent the large contributions to $\mathfrak{S}_2$ originating from the diagonal matrix elements of $\hat S$. This can be achieved, for example, by performing the experiment with oriented systems and applying the HCP field in the direction for which $\langle S\rangle = 0$. Such a condition is always possible to achieve for systems which contain C_s as their symmetry subgroup and is quite common. Under this condition also σ_S^2 is weakly dependent on the geometry.

Is it possible to devise a measurement that exclusively probes the cumulant density matrix ${}^2\Delta$? Our answer to this question is negative, based on the fact that the generating functional for the cumulant and the reduced density matrices

$$
G(J) = \langle\psi_0| O\left(e^{\sum_k J_k \hat c_k^\dagger + J_k^* \hat c_k}\right) |\psi_0\rangle \qquad (9)
$$

is different from the bosonic-like generator of the evolution operator (1). In other words, in order to probe the fermionic RDMs one needs a direct coupling to fermionic degrees of freedom as the Grassmann variables J_k in Eq. (9) realize.

Nonetheless, we will demonstrate below using two numerical examples that the survival probability is a versatile measure of electronic correlations and will compare it to other proposed measures of electronic correlations and entanglement.

III. MEASURES OF ELECTRONIC CORRELATION AND ENTANGLEMENT

It was shown by Juhász and Mazziotti [35] that the Frobenius norm of the second cumulant matrix $[||{}^2\Delta||_F^2 = \mathrm{Tr}[({}^2\Delta)^2]]$ possesses a number of properties that make it a useful measure. $||{}^2\Delta||_F$ scales linearly with the system size and vanishes for single-determinant states. Although it is well suited to compare different configurations of the same system such a measure is less suited to compare different systems as its upper limit is not known.

Here comes informational measures into play, e.g., *von Neumann entropy*. The entropies based on the 1-RDM have been widely studied. Less known are the entropies based on 2-RDM. Carlen and Lieb [36] considered recently the bipartite fermionic states and proved several bounds for the entropy based on ${}^2D$. For a Hilbert space of the $\mathcal{H}_1 \otimes \mathcal{H}_2$ Hamiltonian and corresponding ρ_{12} density matrix the von Neumann entropy can be computed as

$$
S_{12} = -\mathrm{Tr}\rho_{12} \log \rho_{12},
$$

where the trace is understood in the sense of the tensor product $\mathcal{H}_1 \otimes \mathcal{H}_2$. The 2-RDM of a N-particle fermionic system can be considered as a density matrix of a bipartite fermionic state. For this case the following bounds are known (cf. Carlen and Lieb [36])

$$
S(\rho_{12}) \geqslant 2 \ln N + O(1), \qquad (10)
$$

$$
2S_1 - S_{12} \geqslant \ln\left(\frac{2}{1 - \mathrm{Tr}\rho_1^2}\right) \geqslant \ln\left(\frac{2}{1 - e^{-S_1}}\right). \qquad (11)
$$

In the following we compare different correlation measures and numerically verify the inequalities.

Applications

All results so far were represented in some abstract one-particle basis. In what follows we will focus on molecular systems with equal number of spin-up (N_α) and spin-down (N_β) electrons. To treat such systems it is convenient to work in the closed shell Hartree-Fock (RHF) molecular orbital (MO) basis, distinguish spin-up and spin-down MO states, and to denote them as i and $\bar i$, respectively. This implies some additional symmetries. Obviously ${}^1D^i_j = {}^1D^{\bar i}_{\bar j}$ and ${}^1D^i_{\bar j} = {}^1D^{\bar i}_j = 0$, and we have the following blocks for the 2-RDMs:

$$
{}^2D^{ij}_{kl} = {}^2D^{\bar i\bar j}_{\bar k\bar l}, \quad {}^2D^{i\bar j}_{k\bar l} = {}^2D^{\bar i j}_{\bar k l}, \qquad (12)
$$

and the same holds for the cumulants. Since 2-RDMs in Eq. (12) are obtained as scalar products of the $c_i c_j|\psi\rangle$ and $c_i c_{\bar j}|\psi\rangle$ vectors we will denote these blocks as AA and AB. Other 1- and 2-RDMs are obtained by the use of anticommutation relations. In order to emphasize spin degrees of freedom we separately compute the electronic correlation measures associated with AA and AB blocks.

For the computation of entropies the density matrices must be normalized to have trace equal to one. Thus, we introduce

$$ {}^1\tilde{D}^i_j = \frac{1}{N_\alpha}\,{}^1D^i_j, \tag{13}$$

$$ {}^2\tilde{D}^{ij}_{ij} = \frac{1}{N_\alpha(N_\alpha-1)}\,{}^2D^{ij}_{ij}, \quad {}^2\tilde{D}^{i\bar{j}}_{i\bar{j}} = \frac{1}{N_\alpha N_\beta}\,{}^2D^{i\bar{j}}_{i\bar{j}}, \tag{14}$$

with $\mathrm{Tr}[{}^1\tilde{D}] = \sum_i {}^1\tilde{D}^i_j = 1$, $\mathrm{Tr}[{}^2\tilde{D}] = \sum_{ij} {}^2\tilde{D}^{ij}_{ij} = 1$, and $\mathrm{Tr}[\,{}^2\tilde{D}] = \sum_{ij} {}^2\tilde{D}^{i\bar{j}}_{i\bar{j}} = 1$.

Carlen and Lieb showed [36] that the inequalities (10) and (11) are saturated for single Slater determinant states. In fact, it can be verified that boundary values are achieved for each spin channel separately. For single determinant states the cumulant matrix ${}^2\Delta$ vanishes and 2-RDM is given by its unconnected components ${}^2D^{ik}_{jl} = {}^1\Delta^i_j \wedge {}^1\Delta^k_l$. Specifically, ${}^2D^{ik}_{jl} = f_i f_k(\delta_{ij}\delta_{kl} - \delta_{il}\delta_{jk})$ and ${}^2D^{i\bar{k}}_{j\bar{l}} = f_i f_{\bar{k}}\delta_{ij}\delta_{\bar{k}\bar{l}}$ in the AA and AB channels. The first matrix has $N_\alpha(N_\alpha-1)/2$ nonzero eigenvalues equal to 2, whereas the second one has $N_\alpha N_\beta$ nonzero eigenvalues equal to 1. Correspondingly, the entropies in each channel are $S^0_{AA} = \log\frac{1}{2}N_\alpha(N_\alpha-1) = 2\log N_\alpha + O(1)$ and $S^0_{AB} = \log N_\alpha N_\beta$. In the next section we will plot the entropies with respect to these reference values.

IV. NUMERICAL ILLUSTRATIONS

We consider two simple multielectron systems, the LiH molecule (Figs. 1 and 2) and the H_6 ring (Figs. 3 and 4) and study how different correlation measures vary when the system deviates from equilibrium geometries. We use our implementation [37,38] of the algorithm by Olsen *et al.* [39] based on the graphical unitary group approach [40] for performing full CI calculations and subsequent determination of 2-RDMs, coupled cluster and multireference calculations are carried out with the GAUSSIAN 03 program. The systems represent two different scenarios of electronic correlations adopted in quantum chemistry. The diatomic molecule is a typical system with importance of *dynamic* correlations. Numerous Slater determinants contribute to the correlation energy, however, *one* of them is dominant. Thus, even for stretched geometries the Hartree-Fock (HF) solution represents a valid starting point for treating electronic correlations with single-reference methods [41]. This is not so for the H_6 ring for which *static* correlations are important. Even for slight deviations from the equilibrium the wave function of the system takes a form of a sum of several equally significant Slater determinants. It was shown by Bénard and Paldus [42] that restricted HF solutions are unstable with respect to spin-unrestricted perturbations for a wide range of geometries. This invalidates the restricted Hartree-Fock approach and also all the single-reference correlated methods based on it. At the same time it poses an interesting question on whether such spin instabilities could be detected by some correlation measures.

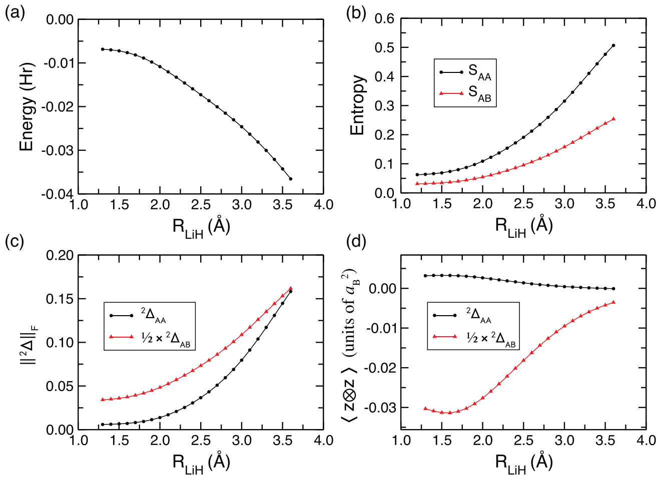

FIG. 2. (Color online) Full CI calculation for the stretched LiH molecule performed with the 6-311++G($2d$,$2p$) basis set, 20 molecular orbitals are included in a correlated treatment. The electron correlation increases monotonically as the bond is stretched. This is manifested in the correlational energy (a), the entropies (b), the Frobenius norm of the second cumulant matrices (c), and the expectation value of the $z \otimes z$ operator [cf. $\langle[\hat{S}\otimes\hat{S}]\rangle$ in Eq. (7) or $\sum_{ijkl} S_{ij} S_{kl}{}^2\Delta^{ik}_{jl}$ in Eq. (8)] (d). The entropies are given with respect to the single determinant values S^0_{AA} and S^0_{AB}.

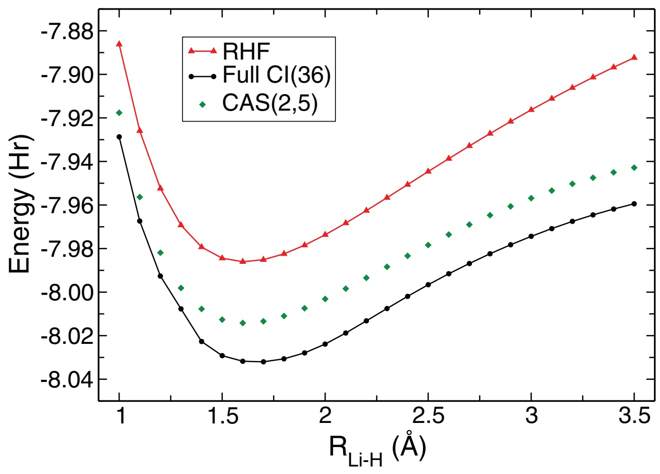

FIG. 1. (Color online) Potential energy surfaces for the stretched LiH molecule.

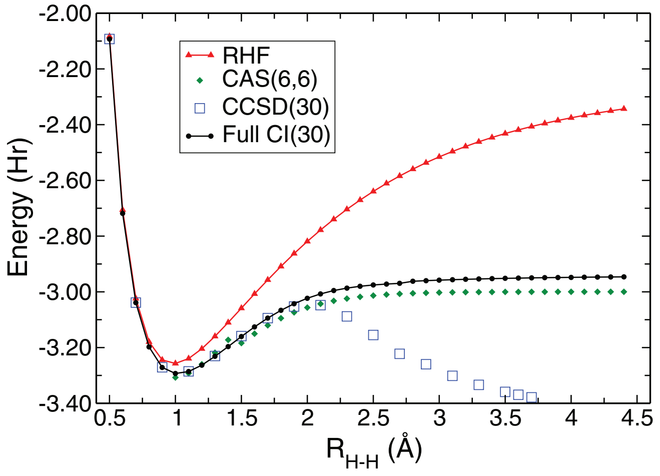

FIG. 3. (Color online) Potential energy surfaces for the symmetrically stretched H_6 molecule.

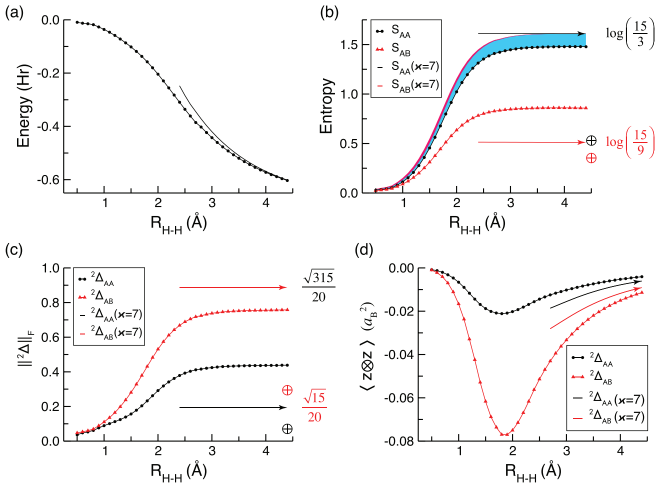

FIG. 4. (Color online) Full CI calculation for the stretched H_6 ring molecule performed with *aug-cc-pvqz* basis set, 30 molecular orbitals included in a correlated treatment. The electron correlation increases monotonically as the bonds are stretched. This is manifested in the correlational energy (a), the entropies (b), the Frobenius norm of the second cumulant matrices (c), and the expectation value of the $z \otimes z$ operator [cf. $\langle[\hat{S} \otimes \hat{S}]\rangle$ in Eq. (7) or $\sum_{ijkl} S_{ij} S_{kl} {}^2\Delta_{jl}^{ik}$ in Eq. (8)] (d). The entropies are given with respect to the single determinant values S^0_{AA} and S^0_{AB}. Thin lines with arrows denote results for $\varkappa = 7$ state. Notice that this state was only computed for larger interatomic distances where it becomes indistinguishable from the ground state (see the energy plot). Blue and red shading stands for the first and second Carlen-Lieb bound [Eq. (11)]. Black and red circles denote results for the $3H^-$ asymptotic state.

Let us consider first a simpler case of a *single bond breaking*. It can be easier treated with quantum chemistry methods as compared, e.g., with double bond breaking in O_2, C_2, or triple bond breaking in N_2 dimers. However, the physical mechanisms are the same. LiH possesses only four electrons (in $1\sigma^2 2\sigma^2$ configuration of the ground $^1\Sigma^+$ state) which makes it well suited for exact diagonalization studies. For these rather small full electron calculations we used the 6-311++G($2d$,$2p$) basis set yielding a total of 37 basis functions. Even with $(6s2p)/[4s2p]$ contracted basis functions for the H atom and $(12s6p2d)/[5s4p2d]$ contraction for the Li atom it is capable of representing a substantial portion of the correlation energy (Fig. 1). We used the augmented *cc-pv5z* basis set for the verification of our results. Stretching the molecule (the equilibrium distance is 1.6 Å based on a CCSD calculation) leads to the breaking of a single covalent bond and to an increase of the correlation energy (Fig. 2). Our simulations indicate similar behavior for the entropies and norms of the second cumulant matrices. Notice that the molecule is in the singlet ground state and therefore there are only two independent spin blocks: ${}^2\Delta_{BB} = {}^2\Delta_{AA}$, ${}^2\Delta_{BA} = {}^2\Delta_{AB}$. If HCP has the electric field vector aligned perpendicular to the molecule's axis (in z direction) the expectation value of the dipole moment vanishes ($\langle z\rangle = 0$) and we are in the situation analyzed above. The correlated part of the survival probability is given by the expectation value of the $z \otimes z$ two-particle operator and is also computed in AA and AB channels (Fig. 2). Its dependence on the interatomic distance is determined by two factors: the norm increase of ${}^2\Delta$ and the matrix elements reduction of the dipole operator. The latter dominates the behavior at large internuclear separations.

Let us look now at the manifestly *multireference system*, the H_6 ring, and investigate how the correlation measures depend on a single geometric parameter, the nearest neighbor distance $R_{\text{H-H}}$. Notice that such symmetric distortion represents a somewhat artificial situation as the dimerized state possesses a lower ground state energy. Multireference SCF in the subspace of six electrons and six orbitals is capable of recovering a major part of the correlation energy and also correctly predicts the asymptotic state of six unpaired electrons residing on six independent H atoms. In contrast, the RHF method which assumes that each molecular orbital is doubly occupied cannot produce such an asymptotic state and fails shortly above the equilibrium distance. Even more drastic divergence shows the single reference coupled cluster approach. In fact, it does not even converge beyond $R_{\text{H-H}} = 3.6$ Å. On the same Fig. 3 results of full CI are shown. The potential energy curve runs almost parallel to MCSCF, however, has a slightly higher energy because not all molecular orbitals (only 30) were included in the calculation. Both methods nicely converge towards the asymptotic energy of -3 hartree. We use the augmented *cc-pqz* basis in the $(7s4p3d2f)/[5s4p3d2f]$ contraction. The survival probability was computed for the case of electric field perpendicular to molecular plane, the expectation value of the dipole moment is zero ($\langle z\rangle = 0$). Correlation energy of this system increases steeply as a function of H-H distance. The norms of the second cumulant matrix and the entropies behave similarly. As in the case of LiH, the expectation value of the direct product $z \otimes z$ is governed by two counteracting factors: increasing ${}^2\Delta$ and reduction of $\mathbf{z}$. At first sight the spin instability is not manifested clearly in these correlational measures. They show essentially the same dependence (up to some scaling) for AA and AB blocks. The difference becomes obvious only by comparing with other electronic states that have different spin configurations.

In the asymptotic limits some electronic states of the H_6 system permit analytical treatment. Because of the vanishing electron repulsion, 6H is the asymptotic ground state with four possible values of the total spin. At large $R_{\text{H-H}}$ the atomic orbitals of six H atoms are not perturbed by the interaction with other ions or electrons and each electron is in $1s$ state. Thus, the density matrices can be conveniently computed in this basis. Since $N_\alpha = N_\beta$ each quantum state of such a six electron system is given by a linear combination of the following Slater determinants $|\alpha_1\alpha_2\alpha_3\bar{\beta}_1\bar{\beta}_2\bar{\beta}_3\rangle$, where $\{\alpha_1,\alpha_2,\alpha_3,\beta_1,\beta_2,\beta_3\}$ is a permutation of orbitals 1 to 6 such that $\alpha_1 < \alpha_2 < \alpha_3$ and $\beta_1 < \beta_2 < \beta_3$, i.e., α and β string are written in the lexicographic order. The spin part of the basis functions is indicated by bar for the spin-down states. There are in total $\frac{6!}{3!\cdot 3!} = 20$ such determinants and they can be further divided into four groups with multiplicities $\varkappa = 1, 3, 5, 7$ each containing 5, 9, 5, and 1 state, respectively. All 20 states are degenerate and we consider a particular example of the $\varkappa = 7$ state in which all the Slater determinants enter with the same coefficient. Other spin multiplicity states can be easily constructed as explained in Pauncz [43]. The two-body density matrix is built from combinatorics factors and evaluates as follows:

$$ {}^2D^{ij}_{ij} = -{}^2D^{ij}_{ji} = \tfrac{4}{20}(1-\delta_{ij}), \tag{15a} $$

$$ {}^2D^{i\bar{j}}_{i\bar{j}} = -{}^2D^{i\bar{j}}_{j\bar{i}} = \tfrac{6}{20}(1-\delta_{ij}), \tag{15b} $$

and vanishes otherwise. Tracing AA or AB blocks leads to the same one-particle density matrix

$$ {}^1D^i_j = \frac{1}{N_\alpha - 1}\sum_{k=1}^{6} {}^2D^{ik}_{jk} = \frac{1}{N_\beta}\sum_{k=1}^{6} {}^2D^{i\bar{k}}_{j\bar{k}} = \frac{1}{2}\delta_{ij}. \tag{16} $$

It is clear that ${}^1Q^j_i = \langle \hat{c}_j \hat{c}^\dagger_i \rangle = {}^1D^i_j$ and ${}^1Q^i_{\bar{j}} = {}^1D^i_{\bar{j}} = 0$. One verifies that the expectation value of the total spin squared operator indeed corresponds to the multiplicity $\varkappa = 2\cdot 3 + 1 = 7$:

$$ \langle \hat{\mathcal{S}}^2 \rangle = \left\langle \hat{\mathcal{S}}_- \hat{\mathcal{S}}_+ + \hat{\mathcal{S}}^2_z + \hat{\mathcal{S}}_z \right\rangle \overset{\langle \hat{\mathcal{S}}_z \rangle = 0}{=} \left\langle \sum_i c^\dagger_{\bar{i}} c_i \sum_j c^\dagger_j c_{\bar{j}} \right\rangle $$

$$ = N_\beta - \sum_{i,j=1}^{6} {}^2D^{j\bar{i}}_{i\bar{j}} = 12. \tag{17} $$

The cumulant matrix is easily evaluated

$$ {}^2\Delta^{ij}_{ij} = -{}^2\Delta^{ij}_{ji} = -\tfrac{1}{40}(1-\delta_{ij}), \tag{18a} $$

$$ {}^2\Delta^{i\bar{j}}_{i\bar{j}} = \tfrac{1}{40} - \tfrac{6}{40}\delta_{ij}, \tag{18b} $$

$$ {}^2\Delta^{i\bar{j}}_{j\bar{i}} = -\tfrac{6}{40} + \tfrac{1}{40}\delta_{ij}. \tag{18c} $$

This yields the norms $||{}^2\Delta_{AA}||_F = \frac{\sqrt{15}}{20}$ and $||{}^2\Delta_{AB}||_F = \frac{\sqrt{315}}{20}$. The expectation values of $z \otimes z$ with respect to ${}^2\Delta_{AA}$ and ${}^2\Delta_{AB}$ are zeros because the dipole transition moments between $1s$ states vanish due to symmetry as manifested in the selection rules. Notice that for finite distances there is a hybridization between these and higher angular momentum states. Therefore, $z \otimes z$ can be different from zero.

The eigenvalues of the matrices [Eqs. (15)] are $w^{AA}_{1,\dots,15} = \frac{1}{15}$, $w^{AA}_{16,\dots 36} = 0$ and $w^{AB}_{1,\dots,15} = \frac{3}{15}$, $w^{AB}_{16,\dots 36} = 0$. After the normalization we obtain the pair entropies $S_{AA} = S_{AB} = \log 15$. Similarly, the entropies can be computed from the 1-RDM, $S_A = S_B = \log 6$.

Another interesting case is in which the system dissociates into three hydrogen anions (H^-) and three protons. This is an excited 20-fold degenerate, yet bound state of the system with the binding energy of just 3×0.7542 eV $= 3 \times 0.0277$ hartree (measured with respect to the energy of three neutral H atoms). The state is extremely correlated with RHF not being capable of yielding the negative energy (for an overview on the electronic structure of H^- we refer to Rau [44], in particular we quote from this work: "The (wave-) function exhibits a radial 'in-out' correlation between the electrons such that when one electron is 'in' close to the nucleus, the other is kept 'out.' "). We can also view H^- as a partial case of the He isoelectronic series with the nuclear charge Z being very close to the critical value $Z_{\mathrm{crit}} \approx 0.911$ at which "a quantum phase transition" from a bound to an unbound two-electron system occurs. A detailed analysis of this system was performed in the context of strictly correlated-electrons functional [45]. The fact that there are just two electrons in the system allows us to exactly compute the Kohn-Sham (KS) potential by simple inversion of the KS equation [46]. The KS molecular orbitals are eigenfunctions of the noninteracting Schrödinger equation. For the singlet $\varkappa = 1$ two-electron state there is a one-to-one correspondence between the exact density and the Kohn-Sham orbitals $\psi(\mathbf{r}) = [\frac{\rho(\mathbf{r})}{2}]^{1/2}$. Even though the KS potential can be explicitly constructed, the density functional theory does not permit us to find the off-diagonal elements of 1-RDM. Therefore, we use again the full CI approach. It is sufficient to diagonalize the Hamiltonian for a single H^- atom (for such a system the larger *aug-cc-pv6z* basis set can be used) and to construct the ${}^2\Delta$ for the total system by the observation that it is given by a direct sum of the cumulant matrices of each subsystem. In order to compute the entropies we reconstruct the 2-RMD from the cumulant matrix and using the fact that 1-RDM is nonzero only when both indices denote states of the same H^- anion.

Numerical results for different correlation measures are shown at Fig. 4 for the ground state together with the asymptotic values for the $\varkappa = 7$ state (obtained analytically) and for the $3\mathrm{H}^-$ state. The latter is based on the full CI treatment of H^- and is only valid for $R_{\text{H-H}} \to \infty$. For finite distances there is a coupling between the subsystems and one needs to diagonalize the full Hamiltonian. This is, however, a formidable task since $3\mathrm{H}^-$ is a highly excited state of the system not amenable to the Lanczos diagonalization.

The blue shaded area on the entropy plot shows the difference between the exact value of the two-particle entropy and the first Carlen and Lieb estimate, $2S_1 - \ln(\frac{2}{1-\mathrm{Tr}\rho_1^2})$. The red shaded area illustrates the second Carlen and Lieb inequality, $2S_1 - (\frac{2}{1-e^{-S_1}})$. Since at the asymptotic limit the 1-RDM and, therefore, S_1 and $\mathrm{Tr}\rho_1^2$ are the same for all 20 degenerate states, the same inequalities hold for all of them. $\varkappa = 7$ state saturates the inequalities and hence has the largest possible two-particle entropy among these states. $3\mathrm{H}^-$, on the other hand, has the smallest entropies and Frobenius norms out of all states that we considered. For them correlational measures lie in between these extremes. In fact, all three of them are capable of discriminating between the spin configurations. The survival probability which is closely connected to the averaged value of $z \otimes z$ can even be measured experimentally. In contrast, the 1-RDM and all associated correlational measures are ignorant to the spin configuration as the example of the asymptotic 6H states shows. Finally, we note the correlation between the saturation behavior seen in Figs. 4(b) and 4(c) when $R_{\text{H-H}}$ is increased beyond ≈2.5 Å and the flatness at these distances of the corresponding potential energy surface, depicted in Fig. 3. Even though the electrostatics is less relevant at these distances, the nonlocal nature imposed by the (anti)symmetry on the total wave function persists for the isolated expanding system. This means, on the other hand, that the asymptotic values of the entropy and $||{}^2\Delta||_F$ delivers short-range (atomistic) information. This picture might change in a nontrivial way when coupling the electronic and the ionic system to external baths, in particular if the bath implies some spin-flip scattering.

V. CONCLUSIONS

We explored theoretically the possibility of accessing the electron correlations using a pump-probe technique with half-cycle pulses. The nonresonant kick-type excitation is appropriate in so far as it allows for many-particle excitations and can still be amenable to quasianalytical treatment. We demonstrated that to the leading order in the field intensity, the probability for a system to remain and/or recur to the initial state (the survival probability) can be expressed in terms of 2-RDM and, hence, represents a measure for electronic correlations. Exact diagonalization studies were performed on two molecules LiH and H_6—prototypes of systems with importance from the point view of dynamic and static correlations. In the dissociative limit the second system permits an analytical treatment of some electronic (asymptotic) states for which different correlational measures and entanglement entropies were computed. Even though these asymptotic subsystems can be considered as noninteracting, the states are entangled due to the wave function antisymmetry. This is reflected in the two-particle entropy, the Frobenius norm of the second cumulant matrix $||^2\Delta||_F$, and in the expectation value of the $z \otimes z$ operator. The latter can be inferred from the proposed measurement of the survival probability. Thus corresponding experiments can probe the spin configuration of many-body systems.

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[33] There are actually two rules under this name. We are talking here about the expression for the total probability which is obtained from the rate equation by the integration with the frequency profile of the excitation pulse.
[34] We note by passing that the quantities which are defined here are of a general nature. In fact, in solids a drastic change in electronic properties may occur upon driving the lattice by an external field, as confirmed by series of recent experiments (albeit not dedicated to the quantity we are discussing here, the survival probability [47]).

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