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# Nonadiabatic response of a finite fermion system to a time perturbation

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The nonadiabatic response to a time perturbation applied to a finite system modeled with the Hubbard Hamiltonian has been investigated in the case where one atom of the cluster is continuously uncoupled (monofragmentation . . . ). An exact solution has been derived using numerical procedures for the octahedron cluster in the $(4\uparrow, 4\downarrow)$ electronic configuration. A comparison of the time evolution of the population $n(t)$ on the moving atom has been carried out between our exact result and the so-called "one-determinant method," which is based on the propagation of only one Slater determinant. An analysis of the discrepancy between the two results is illustrated on the dimer case $AB$ $(A \neq B)$ in the $(1\uparrow, 1\downarrow)$ configuration. The calculations show that more excitations are occurring in the exact calculation leading first to a more efficient initial filling of the uncoupled atom population and secondly to a smaller value of $n(t)$ at the end of the process $(n_f)$. The electronic correlation modifies the dynamics of the process but slightly $n_f$.

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## I. INTRODUCTION

In the past years, experiments on cluster or on solid at the scale of the femtosecond give new interest to the fundamental problem of the time dependent response theory where nonadiabatic phenomena are important. Some time-dependent works have been published recently. We mention some of them: (1) several laser-induced ultrafast phase transitions have been observed[1–3] where interesting transitions between two crystalline structures could occur, (2) the excitation of the electrons in aggregate interacting with rapid charged monoatomic ion where ionization and capture could occur;[4] and (3) femtosecond neutralization dynamics in cluster-solid surface collisions.[5] In the case of the ion-cluster collision, two main procedures have been used: either a semiclassical limit of a time dependent Hartree-Fock description[6] or a time dependent density functional approach[7] to tackle problems involving large cluster, but in principle such procedures do not treat quite well the nonadiabatic response. Theoretical analysis have been carried out: for the case of the analysis of the laser induced femtosecond graphitization of diamond[8] or in the electron emission yield of charged clusters colliding with different surfaces at low energies.[9]

Let us mention another kind of time-dependent work which deals with nanostructures. An electron wave packet[10] is generated in a potential well and oscillates between the sides of the well. At each oscillation the electrons cross a two-barrier heterostructure and a charge $Q(t)$ increasing with time is progressively trapped inside it. This charge reacts on the moving electrons and at large time a chaotic behavior is reached.

In most of the experimental results mentioned above the theoretical analysis was made in a one determinant method (1DM) where the determinant is made up of the time-dependent one-electron wave functions corresponding to the levels filled at $t=0$. In this paper we want to show that a good description of such violent excitations can be reached only by developing the time-dependent $N$-electron wave function on a basis of $N$-electron determinants. This point will be shown by comparing the 1DM results to exact results obtained with a complete determinants basis (CDB) calculation performed on a relatively small 6-atom cluster.

Let us notice that practically the use of CDB method is limited to small aggregates (because the size of the basis increases exponentially with the number of cluster atoms $N$) but clusters with $N>10$ can be studied with a truncated determinant basis. In this cases a control of the validity of the truncation process is necessary.[11–13]

A general question remains to be discussed about the extension to any size of effects obtained for a small system. Let us consider the core photoemission process which is characterized by the sudden appearance of localized strong attractive potential on a deep atom level. For aggregates, the nonadiabaticity of the electron response appears in the photoemission spectrum as shakeup satellite rays at the low energy side of the main ray. In bulk systems, the corresponding feature is an asymmetry of the main ray toward low energies. Thus the shape of the photoemission spectrum changes with the size (which is obviously due to the discreteness of the electron level distribution) but the relative importance of the nonadiabatic part in the spectrum (which can be measured by the ratio between the main and the satellites) does not change much with $N$.

In the present problem we will relate the differences between the 1DM and the CDB method to a physical event: the cancellation at a given time of some atomic weights in the molecular wave functions. As it is likely that such events occur for any cluster sizes, we may think that our conclusion on the preference to be given to the CDB method, drawn from a six-atom study, is valid for any cluster size.

We consider an octahedral six-atom cluster with an $s$ atomic wave function centered on each site. We use the usual form of the Hubbard Hamiltonian to describe the electronic structure

$$H=-\lambda \sum_{\substack{\langle i,j\rangle \\ \sigma}} c^{+}_{i,\sigma} c_{j,\sigma} + U \sum_{i} n_{i,\uparrow} n_{i,\downarrow}, \tag{1}$$

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where the first term describes the hopping between two nearest neighbors ($\lambda=$ the hopping integral). $c^{+}_{i,\sigma}$ ($c_{i,\sigma}$) are the creation (annihilation) operators of an electron on site $i$ with spin $\sigma$. The other term in $H$ is the intrasite electronic interaction ($n_{i,\sigma}=c^{+}_{i,\sigma}c_{i,\sigma}$); $U$ is the intra-atomic electronic correlation. For $U=0$ (i.e., the free electron case), the one-electron levels of $H$ are $-4\lambda$ (non-degenerate), $0\lambda$ (threefold degenerate), and $2\lambda$ (twofold degenerate). In the present article we investigate the six-atom cluster with the octahedron shape and with eight electrons in the electronic configuration (4↑, 4↓) to avoid all problems of degeneracy of the initial state (in this configuration the level structure is complete). Such type of systems can be regarded as describing the $\pi$ electrons in negatively charged or doped carbon molecules.

To analyze the effect of the time-dependent perturbation, we expand the ground-state wave function of the system on all the atomic determinants $\Phi_i$ with six atoms and with the electronic configuration (4↑, 4↓) (the basis size is 215):

$$|\Psi(t=0)\rangle=\sum_i \alpha_i(t=0)|\Phi_i\rangle. \tag{2}$$

Then we have to propagate the wave function by using the Schrödinger equation

$$i\hbar\frac{\partial|\Psi(t)\rangle}{\partial t}=H(t)|\Psi(t)\rangle. \tag{3}$$

The problem is reduced to finding the time evolution of the $\alpha_i$ coefficients. In our case we are led to solve a system of 215 complex differential equations.

## II. PRELIMINARY STUDY OF A TWO-ATOM CASE

Before giving our results on the octahedron we will discuss the dimer case $AB$ ($A\neq B$) with the electronic configuration (1↑, 1↓) where an analytical solution is possible and which illustrates well the differences between the approximate and the exact solutions. We call $\varphi_A$ and $\varphi_B$ the atomic wave functions centered on atoms $A$ and $B$ and $\phi_{1\sigma}(t)=\alpha(t)\varphi_{A\sigma}+\beta(t)\varphi_{B\sigma}$ the molecular ground state. In the 1DM the two electron wave function is given by the propagation of $\det(\phi_{1\uparrow}(t),\phi_{1\downarrow}(t))$ using Eq. (3). The time evolution is controlled by $\alpha(t)$ and $\beta(t)$ which are derived from the following differential equation:

$$i\hbar\begin{bmatrix}\dfrac{\partial\alpha}{\partial t}\\[2ex] \dfrac{\partial\beta}{\partial t}\end{bmatrix}=H_1(t)\begin{bmatrix}\alpha(t)\\ \beta(t)\end{bmatrix}. \tag{4}$$

$H_1$ is the representation of the Hamiltonian $H$ in the one-electron atomic basis ($\varphi_A,\varphi_B$) which has a dimension of two. With no loss of generality, we can write

$$H_1(t)=\begin{bmatrix}H_{11}(t) & H_{12}(t)\\ H_{21}(t) & H_{22}(t)\end{bmatrix}=\begin{bmatrix}0 & -\lambda\\ -\lambda & E\end{bmatrix}, \tag{5}$$

where $E$ is the atomic energy difference of atoms $A$ and $B$. We observe that the equation for $\alpha(t)$ is governed by

$$i\hbar\frac{\partial\alpha}{\partial t}=H_{11}\alpha+H_{12}\beta. \tag{6}$$

Let us examine the exact treatment; the Hilbert basis $\{\Pi\}$ of the two atom system with the electronic configuration (1↑, 1↓) is of fourth order:

$$|\Psi_1\rangle=\det(\varphi_{A\uparrow},\varphi_{A\downarrow}),\quad |\Psi_2\rangle=\det(\varphi_{A\uparrow},\varphi_{B\downarrow}),$$
$$|\Psi_3\rangle=\det(\varphi_{A\downarrow}\varphi_{B\uparrow}),\quad |\Psi_4\rangle=\det(\varphi_{B\uparrow}\varphi_{B\downarrow}). \tag{7}$$

The wave function is searched like

$$|\Psi(t)\rangle=\alpha_1|\Psi_1\rangle+\beta_1|\Psi_2\rangle+\gamma_1|\Psi_3\rangle+\delta_1|\Psi_4\rangle. \tag{8}$$

Thus the time evolution of the wave function leads to the calculation of the time evolution of the four coefficients ($\alpha_1,\beta_1,\gamma_1,\delta_1$). But if we assume that the 1DM is correct then these four coefficients are related to $\alpha,\beta$, the coefficients derived previously with the 1DM, and at every time they are worth respectively $\alpha^2$, $\alpha\beta$, $-\alpha\beta$, and $\beta^2$. But, moreover, they are constrained to verify Eq. (3), i.e.,

$$i\hbar\frac{d}{dt}\begin{pmatrix}\alpha^2\\ \alpha\beta\\ -\alpha\beta\\ \beta^2\end{pmatrix}=H_2\begin{pmatrix}\alpha^2\\ \alpha\beta\\ -\alpha\beta\\ \beta^2\end{pmatrix}. \tag{9}$$

$H_2$ is the representation of the Hamiltonian $H$ in the basis $\{\Pi\}$

$$H_2(t)=\begin{bmatrix}0 & -\lambda & \lambda & 0\\ -\lambda & E & 0 & -\lambda\\ \lambda & 0 & E & \lambda\\ 0 & -\lambda & \lambda & 2E\end{bmatrix}. \tag{10}$$

Let us examine the differential equation for $\alpha^2$ given by Eq. (9); it leads to

$$i\hbar\frac{\partial\alpha^2}{\partial t}=i\hbar 2\alpha\frac{\partial\alpha}{\partial t}=2\alpha\{H_{11}\alpha+H_{12}\beta\}. \tag{11}$$

Therefore, if $\alpha$ is not equal to zero, we can divide by $\alpha$ in Eq. (11) and we obtain for this quantity the same equation as in the 1DM. But if $\alpha$ can go to zero, the division by zero is incorrect and the two methods give different results. The schematic behavior for the two methods applied to previous conclusions obtained for the dimer can be straightforwardly generalized to larger clusters by saying that a difference between the two methods can be expected when one of the $\alpha_i(t)$ coefficients (i.e., the atomic weight on one of the molecular wave functions) goes to zero.

## III. RESULT FOR THE SIX-ATOM CLUSTER CASE

To illustrate our previous result, we study the nonadiabatic response of a cluster submitted to a time dependent

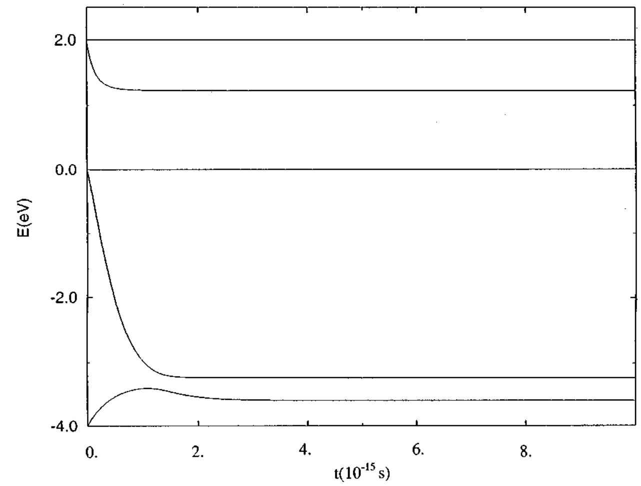

FIG. 1. Time dependence of the adiabatic eigenvalues (eV) for a kinetic energy $E_K = 1$ keV of the moving atom.

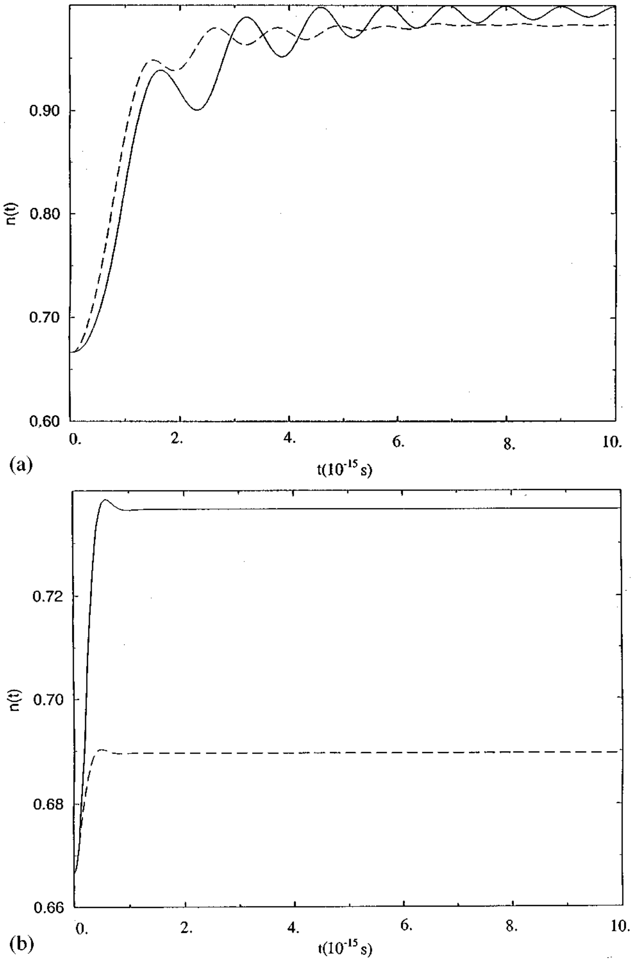

FIG. 2. Time evolution of the population per spin on the leaving atom [exact calculation (---); one determinant method (—)] for the free electron case ($U = 0$ eV): (a) $E_K = 10$ eV; (b) $E_K = 10$ keV.

perturbation. Let us consider the case where one atom of the cluster is continuously uncoupled (i.e., the bond between the atom and the remaining cluster is broken) such that the hopping integral λ between the atom and its nearest neighbors is time dependent with the following expression:

$$\lambda = \lambda_0 \exp(-\eta t) \tag{12}$$

and the energy on the uncoupled atom is

$$E = (E_f - E_{\rm at})[1 - \exp(-\eta t)] + E_{\rm at}, \tag{13}$$

where $E_{\rm at}$ is the atomic level and $E_f$ is the energy at the end of the process. We have chosen this kind of time evolution because it describes the sputtering phenomena[11] or the monofragmentation of an atom from a cluster after a sudden perturbation has excited the cluster (laser, collision, etc.). The parameter $\eta$ is linked to the velocity $v_\perp$ of the uncoupled atom by

$$\eta = \gamma v_\perp, \tag{14}$$

where $\gamma^{-1}$ is a characteristic distance of about 0.2 nm. We also introduce a kinetic energy $E_K = \frac{1}{2} m v_\perp^2$ with $m$ equal to the carbon mass.

Let us investigate the case where one of the atoms of the octahedron in the electronic configuration $(4\uparrow, 4\downarrow)$ is uncoupled and its trajectory is radial. As in Ref. 11 we take $E_f - E_{\rm at} = -3.6\lambda_0$ ($\lambda_0$ has been taken equal to 1 eV), which implies that as the atom is moving away it will take an excess of charges. The time evolution of the adiabatic eigenvalues of the Hamiltonian $H(t)$, given in Fig. 1, shows that the degeneracy of the levels is partially removed. The interesting physical quantity during the uncoupling process is the population per spin direction $n(t)$ on the uncoupled atom. At the beginning of the process, all the sites are equivalent and $n(t=0) = 2/3$. Let us report first results for the noninteracting case ($U = 0$). In Fig. 2 the time evolution is displayed for various kinetic energies of the uncoupled atom. The exact method and the 1 DM have been investigated. The two methods give a time evolution and in particular a final limit $n(t=\infty)$ value which are different (the larger the discrepancy, the larger the kinetic energy of the atom). In Fig. 3 the weights on the atomic wave functions of the molecular wave function $\phi_2$ are reported. One of them cancels in the region $2\times10^{-15}\,{\rm s} < t < 6\times10^{-15}$ s; this fact is reminiscent of the effect observed in the dimer calculation and explains why in the same time interval the two methods lead to different results. In the $t = 0$ region the two curves vary as $t^3$ (this point is shown in the Appendix. For large $t$ values, $n(t)$ grows faster in the exact method. After a rapid increase $n(t)$ exhibits an oscillating behavior and finally reaches a constant value $n_f$. Here again the two kinds of results are different, the period of oscillations is larger, and the value $n_f$ is smaller in the exact method. These effects can be understood. As the number of available states is larger in the exact method the transfer of charges from the level on the moving atom and on the remaining part of the molecule is more efficient and rapid charge exchanges occur. The second effect comes from the fact that the levels on the remaining part of the molecule are globally more excited in the exact calculation; as a consequence the lowest levels have an average number of electrons smaller in the exact calculation and they hardly fill the emitted atom level.

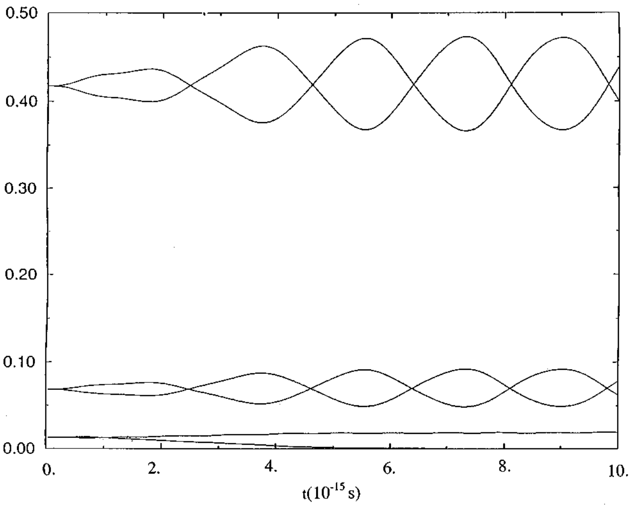

FIG. 3. Time dependence of the weights on the atomic wave functions of the molecular wave function $\phi_2$ ($U=0$ eV).

Let us examine the effect of the kinetic energy $E_K$ of the leaving atom on the excitations of the system. This effect is qualitatively similar for the two methods. In Fig. 4, the weight of the excitations [i.e., the state with one (two, etc.) electron-hole pair] are reported for $E_K=10$ eV. At the beginning there is only one state (the ground state) with a weight of 1 at $t=0$ which decreases for larger time [plot 4(a)]; then the system is excited, excitations with one electron-hole pair appear first [plot 4(b)], then excitations with 2 (3) pairs (plot 4(c) [4(d)]). For higher $E_K$ values, the excitations occur faster with a large number of electron-hole pairs and with a quite large contribution. The fact that the number of excitations is increasing with $E_K$ confirms our analysis on the decrease of $n(t)$ and the increase of the $n(t)$ oscillation frequency with increasing $E_K$.

Now let us examine the effect of the electronic correlation on the process (Fig. 5) for the exact calculation. The oscillations $n(t)$ disappear when $U$ increases. For the same uncoupling condition, the introduction of $U$ tends to slightly decrease the value $n_f$. This is physically due to the fact that the electrons are less mobile and the filling of the emitted atom level is worse.

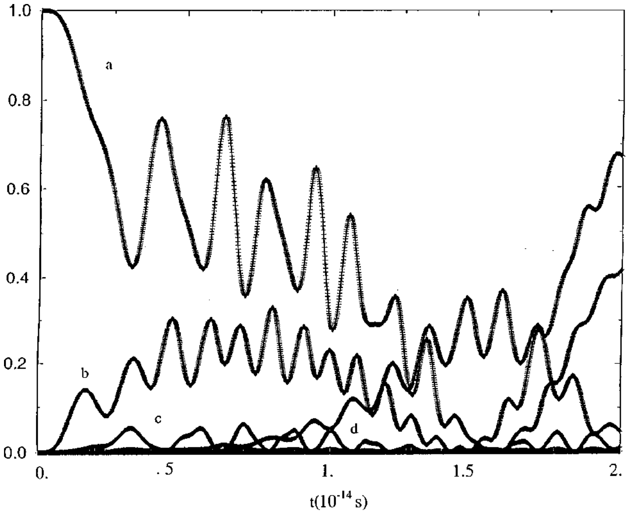

FIG. 4. Time dependence of the weight of the excitations [i.e., states with one (two, three, etc.) electron-hole pairs] for $E_K=10$ eV: the contributions with 0(1,2,3) electron-hole pairs are reported respectively in plots (a) [(b), (c), (d)].

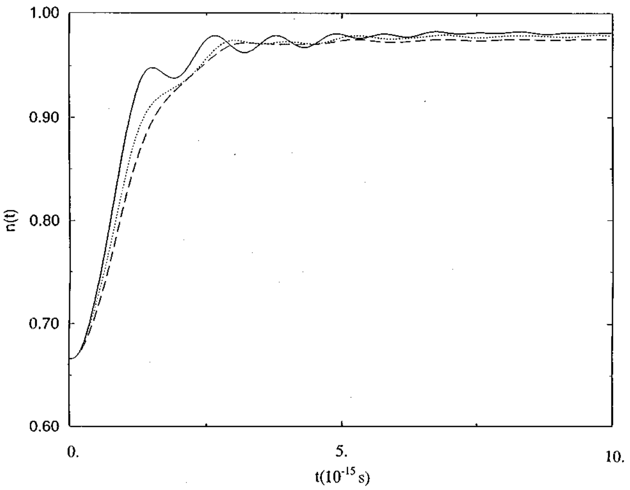

FIG. 5. Exact time evolution of the population per spin on the leaving atom with the kinetic energy $E_K=10$ eV, $U=0$ eV (—), $U=2$ eV (···), and $U=4$ eV (---).

Finally, we investigate the uncoupling case where the energy $E$ is constant ($E=E_{\mathrm{at}}$); only the hopping term has a time dependence. The calculation shows that for $E_K>10$ eV the leaving atom always takes some electron even for large $U$. For $E_K=1$ eV, i.e., for a very slow departure and for $U=5$ eV (Fig. 6) $n(t)$ increases in a first step then decreases to a lower value than the initial one. For the first part of the $n(t)$ evolution, the effect is due to the hopping term but the electrons in the cluster feel an effective electron repulsion which is smaller than the atomic electron repulsion on the atom and so, in the second step they try to jump back

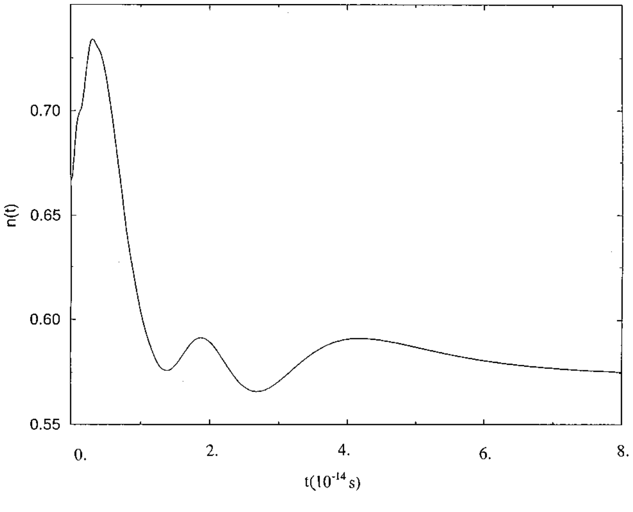

FIG. 6. Exact time evolution of the population per spin on the leaving atom $E_K=1$ keV, $U=5$ eV (the atomic level of the leaving atom has been kept equal to the atomic level of the cluster).

to the cluster to decrease the correlation energy. This effect is appearing for large $U$, but as the effect of $U$ is to decrease the dynamics of the electrons, the jump is only possible for a very small value of $E_K$.

## IV. CONCLUSION

Let us discuss the main results of this work on the monofragmentation type perturbation. Our results show that a 1 DM is badly adapted to these dynamical problems. This remark is valid even when the energy of the incident charge is low ($E_K = 10\,\mathrm{eV}$) since both the $n(t)$ behavior and $n_f$ are strongly different from the exact results. As we discussed before, this remark can be extended to calculations on systems with intermediary sizes (∼100 atoms). It seems that an important improvement can be expected with the use, instead of the 1DM, of a determinant basis correctly truncated as it has been done in previous works.[11–13]

We also observe that the introduction of the relatively large $U$ intra-atomic repulsion energies does not change much the evolution of the final population $n_f$ with $E_K$ though interesting differences appear in the $n(t)$ behavior which can be physically understood.

The present article deals with a finite cluster which has some attraction (use of the exact diagonalization method), nevertheless let us mention that there are some problems to extrapolate the predictions obtained with some small cluster calculations to get a reliable understanding of an infinite system due to the appearances of certain scales of energies associated with the cluster size. If we want to study the bulk, an appropriate way will be to embed the cluster.

Let us make a final remark. The discrepancy between the 1DM and the CDB method obtained in this study is more general and could be obtained with other perturbations. Only the magnitude of the discrepancy depends on the studied system.

## ACKNOWLEDGMENTS

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## APPENDIX: $t^3$ DEPENDENCE OF $n(t)$ AT THE BEGINNING OF THE PROCESS

The time dependent Hamiltonian can be recast into the following form:

$$H = H_0 + (1 - e^{-\eta t}) H_3 ,$$

where $H_0$ and $H_3$ are time independent. For the wave function of $H$ is a search with the following perturbation form:

$$\psi = \psi_0 + \psi_R + i\,\psi_i ,$$

where $\psi_0$ is the wave function of the unperturbed system and $\psi_R$ and $\psi_i$ the real and imaginary part of the perturbed wave function.

Therefore from Eq. (3) we have the following relations:

$$\begin{aligned} i\hbar \frac{d\Psi_R}{dt} - \hbar \frac{d\Psi_i}{dt} &\\ = H_0(\Psi_0 + \Psi_R) + iH_0\Psi_i + (1 - e^{-\eta t}) H_3 \Psi_0 &\\ + (1 - e^{-\eta t}) H_3 (\Psi_R + i\Psi_1). & \qquad \text{(A1)} \end{aligned}$$

For small time. Equation (A1) gives two relations

$$\hbar \frac{d\Psi_R}{dt} = H_0 \Psi_i , \quad \hbar \frac{d^2\Psi_R}{dt^2} = H_0 \frac{d\Psi_i}{dt} .$$

A second order calculation leads to $\psi_R$ and $\psi_i$,

$$\Psi_R = -t^2 \frac{E_0^2}{2\hbar^2} \Psi_0 , \quad \Psi_i = -E_0 \frac{t\Psi_0}{\hbar} - \frac{\eta}{2\hbar} t^2 H_3 \Psi_0 .$$

The second order calculation of the population (i.e., $|\Psi|^2$) on the moving atom leads to the term in $t^2$ being zero.

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