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The decay of excited He from stochastic density-functional theory: a quantum measurement theory interpretation

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Abstract

Recently, time-dependent current-density-functional theory has been extended to include the dynamical interaction of quantum systems with external environments (Di Ventura and D'Agosta 2007 *Phys. Rev. Lett.* **98** 226403). Here we show that such a theory allows us to study a fundamentally important class of phenomena previously inaccessible by standard density-functional methods: the decay of excited systems. As an example we study the decay of an ensemble of excited He atoms, and discuss these results in the context of quantum measurement theory.

(Some figures in this article are in colour only in the electronic version)

Density-functional theory (DFT), in both its ground-state and time-dependent versions [1–5] has become the method of choice to study several equilibrium and non-equilibrium properties of interacting many-particle systems evolving under Hamiltonian dynamics.

There is, however, a large class of physical problems where the dynamical interaction of a quantum system with an external environment needs to be taken into account. To this class of *open quantum systems* belongs also one of the most basic tenets of quantum theory, namely the non-unitary evolution of a quantum state due to the measurement by an apparatus. Non-unitary quantum evolution also pertains to processes where the energy of the quantum system relaxes into the degrees of freedom of a bath, like, e.g., the decay of excited systems. An understanding of such processes from a microscopic point of view would represent a substantial advancement in the study of open quantum systems.

To address the above issues, Di Ventura and D'Agosta have recently proved [6] that given an initial quantum state, and an operator \hat{V} that describes the interaction of a many-body system with a bath, two external vector potentials $\mathbf{A}(\mathbf{r}, t)$ and $\mathbf{A}'(\mathbf{r}, t)$ that produce the same ensemble-averaged current density, $\overline{\mathbf{j}(\mathbf{r}, t)}$, must necessarily coincide, up to a gauge transformation. The above theorem thus extends the previous theorems of dynamical DFT (that are one of its corollaries if $\hat{V} = 0$), and allows for the first-principles description of

the dynamics of open quantum systems via effective single-particle equations. This theory has been named stochastic time-dependent current-DFT (stochastic TD-CDFT) [6, 7].

Here we apply the above theory to a previously inaccessible problem via standard DFT methods: the decay of an ensemble of excited He atoms. In addition, we interpret the results in the context of quantum measurement theory by showing that the interaction with the environment can be viewed as a continuous 'measurement' of the state of the system, thus making a connection between density-functional theory and quantum measurement theory.

We consider two cases: (1) an ensemble of excited He⁺ atoms, whose dynamics can be directly compared with the one obtained from a density-matrix approach, and thus serves as an important numerical test of our procedure. (2) An ensemble of neutral excited He atoms. Our results reveal unexpected features of this problem, like the dampening and modification of high-frequency oscillations during energy relaxation of the ensemble towards its ground state.

The starting point of stochastic TD-CDFT is the stochastic equation of motion of an auxiliary Kohn–Sham (KS) Slater determinant Ψ^{KS} built out of single-particle KS states ϕ_α ($\hbar = 1$)

$$\partial_t \Psi^{\text{KS}}(t) = -i \sum_i \hat{H}_i^{\text{KS}}(t) \Psi^{\text{KS}}(t) - \frac{\tau}{2} \hat{V}^\dagger \hat{V} \Psi^{\text{KS}}(t) + \ell(t) \hat{V} \Psi^{\text{KS}}(t), \quad (1)$$

where

$$\hat{H}_i^{\text{KS}}(t) = \frac{[\hat{p}_i + \mathbf{A}(\hat{r}_i, t)/c + \mathbf{A}_{\text{xc}}(\hat{r}_i, t)/c]^2}{2} + V_{\text{ext}}(\hat{r}_i) + \hat{V}_{\text{H}}(\hat{r}_i, t), \quad (2)$$

with $\mathbf{A}(\hat{r}_i, t)$, an arbitrary external vector potential, $\mathbf{A}_{\text{xc}}[\bar{\mathbf{j}}(\mathbf{r}, t'), |\Psi_0\rangle, \hat{V}]$ the exchange–correlation vector potential (which is a functional of the average current density $\bar{\mathbf{j}}$, for $t' \leq t$, the initial condition $|\Psi_0\rangle$, and the operator \hat{V}), $V_{\text{ext}}(\hat{r}_i)$ an external scalar potential (e.g., the electron–ion potential), and $\hat{V}_{\text{H}}(\hat{r}_i, t)$ the Hartree potential. The quantity τ has dimensions of time. Without loss of generality the stochastic process, $\ell(t)$, is chosen such that it has both zero ensemble average and δ -autocorrelation, i.e.¹,

$$\overline{\ell(t)} = 0; \overline{\ell(t)\ell(t')} = \tau\delta(t - t'), \quad (3)$$

where the symbol $\overline{\dots}$ indicates the average over a statistical ensemble of identical systems all prepared in the same initial quantum state $|\Psi_0\rangle$. For the particular choice of bath operator we will make in this paper (equation (5)), which acts on single-particle states only, the stochastic equation (1) is simply

$$\partial_t \phi_\alpha(t) = -i\hat{H}_{\text{KS}}\phi_\alpha(t) - \frac{\tau}{2}\hat{V}^\dagger\hat{V}\phi_\alpha(t) + \ell(t)\hat{V}\phi_\alpha(t), \quad (4)$$

where α contains also the spin degrees of freedom [8].

The use of a stochastic Schrödinger equation in the context of DFT, and not of an equation of motion for the density matrix, is because in DFT the KS Hamiltonians depend on the density (and/or the current density), and therefore they are, in general, different for the different elements of the ensemble (i.e., they are stochastic Hamiltonians). This does not generally guarantee a closed equation of motion for the KS density matrix of a mixed state [6].

As mentioned previously, our aim is to describe the decay of excited electrons bound to a He nucleus. The electrons are prepared in some initial excited state, and evolve into the ground state as a result of the stochastic interaction with an environment, that, quite generally, can be thought of as a boson field with dense spectrum. The precise form of the operator \hat{V} which causes this behavior would, in general, depend on the detailed model of the bath. The operator \hat{V} also determines the rate at which the system relaxes towards equilibrium.

Here we choose the simplest possible operator, whose matrix elements are²

$$\langle \epsilon_i | \hat{V} | \epsilon_j \rangle = \begin{cases} 1/\sqrt{\tau t_d} & \text{if } i = 0, \text{ and } 0 < j < M \\ 0 & \text{otherwise,} \end{cases} \quad (5)$$

where $|\epsilon_i\rangle$ is an eigenstate of the ground-state KS Hamiltonian in the absence of the interaction with the bath, ϵ_i is the

¹ In the calculations of this paper, we use small but finite time steps of duration Δt . The mean and autocorrelation of $\ell(t)$ are thus given by $\overline{\ell(t_i)} = 0$ and $\overline{\ell(t_i)\ell(t_j)} = \delta_{i,j}\tau/\Delta t$, respectively, where t_i and t_j are arbitrary times, and $\delta_{i,j}$ is the Kronecker delta. We have chosen the probability distribution $P(\ell)$ of $\ell(t)$ to be Gaussian, so that $P(\ell) = \sqrt{\Delta t/2\pi\tau}\exp(-\ell^2\Delta t/2\tau)$.

² In our numerical work we have used a position basis so that the action of this operator in this basis is $\langle \mathbf{r} | \mathbf{V} \phi(t) \rangle = \sum_i \langle \mathbf{r} | \epsilon_i \rangle \sum_j \langle \epsilon_i | \mathbf{V} | \epsilon_j \rangle \langle \epsilon_j | \phi(t) \rangle = \langle \mathbf{r} | E_0 \rangle \frac{1}{\sqrt{\tau t_d}} \sum_{j=1}^{j < M} \langle \epsilon_j | \phi(t) \rangle$.

corresponding eigenvalue, and the upper limit M is a given integer representing the number of states we keep in the simulation. (In the present case we have kept $M = 15$ states.) The parameter t_d gives the timescale over which the decay will occur, with larger values of t_d leading to longer decay times. In the following we have taken $t_d = 1$ fs, which is an arbitrary time constant chosen only to illustrate the method with no reference to any particular experiment. The operator \hat{V} defined this way ensures that the stochastic Schrödinger equation (4) is independent of the magnitude of τ .

Clearly, the above operator reduces the projection of a wavefunction from the states $\{|\epsilon_1\rangle, |\epsilon_2\rangle \dots |\epsilon_{M-1}\rangle\}$, and increases the projection onto the ground state $|\epsilon_0\rangle$. Physically, it describes energy relaxation and dephasing.

The linear stochastic Schrödinger equation (4) preserves the ensemble-averaged wavefunction normalization [6]. However, the normalization is not necessarily satisfied for any particular realization of $\ell(t)$. In order to reduce the number of dynamical calculations to perform the ensemble average, we have explicitly re-normalized $|\phi\rangle$ at every time step. This corresponds to the solution of a nonlinear stochastic Schrödinger equation which is equivalent to equation (4). (For a discussion of a similar nonlinear stochastic Schrödinger equation, see [9].) This imposition of normalization is motivated by the intended application of this formalism toward a density-functional calculation, for which repeated calculations are computationally expensive, especially when the number of electrons is large.

We begin by considering the behavior of an ensemble of He^+ ions interacting with the environment represented by the operator (5). For this one-electron case DFT is not required. Nonetheless, it serves as an important numerical test. We prepare the system with all ions in the ensemble in the 2s state, denoted by $|\epsilon_1\rangle$, and then let the electrons evolve in time according to equation (4)³. Panel (a) of figure 1 gives the projections $P_i(t) = |\langle \epsilon_i | \phi(t) \rangle|^2$, as a function of time for one particular realization of $\ell(t)$. We see that the projection $P_0(t)$ onto the ground state approaches one as time evolves, while the projections onto other states approach zero, indicating energy relaxation into the ground state. In order to demonstrate that this behavior is not due to the particular choice of seed in our random number generator, we also plot the projections $P_i(t)$ averaged over 5 different simulations with different seeds. One can clearly see that the fluctuations in panel (b) of figure 1 are reduced in comparison to the fluctuations in panel (a).

For the single-electron case of He^+ , we can analytically treat the ensemble average over all realizations of $\ell(t)$ by considering the density matrix $\hat{\rho}$ of this mixed state. In this case, using equations (4) and (3), it can be shown [15, 6] that the stochastic Schrödinger equation (4) is the unraveling of the following quantum master equation

$$\frac{d\hat{\rho}}{dt} = -i[H_{\text{KS}}, \hat{\rho}] + \tau V \hat{\rho} V^\dagger - \frac{\tau}{2} \hat{\rho} V^\dagger V - \frac{\tau}{2} V^\dagger V \hat{\rho}. \quad (6)$$

³ We represent the He nucleus with a simple $2/r$ potential. We integrate out the singularity at the origin using a method similar to the Ewald method [10, 11]. We use the Hockney method to calculate the potential of an isolated system [12]. The supercell is a cube of length 16.93 Å, and the grid spacing is 0.239 Å. We use the Chebyshev method of constructing the propagator [13, 14], and we use a time step of 0.02 fs.

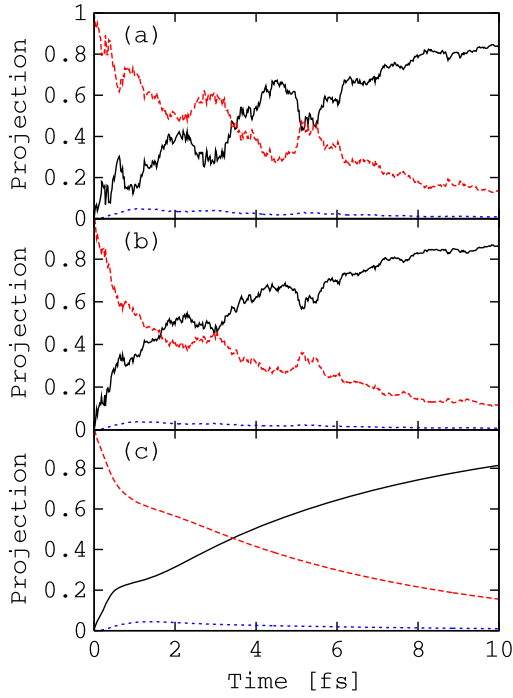


Figure 1. Panel (a): stochastic evolution of the projections P_i onto the unperturbed states ϵ_i , for He^+ , as a function of time. The black (solid), red (dashed), and blue (dotted) curves correspond to P_0 , P_1 , and P_2 , respectively. Note that the projections P_3 and P_4 coincide with P_2 , since all three states have p symmetry. All other projections are vanishingly small. Panel (b): same as for panel (a), but averaged over five different runs, each with a different seed for the random number generator. Panel (c): same as for panels (a) and (b), except that the dynamics were calculated using the Lindblad master equation (6).

In panel (c) of figure 1 we plot the matrix elements $\langle \epsilon_i | \hat{\rho} | \epsilon_i \rangle$ which show the same behavior obtained with equation (4), giving us confidence on the numerics of our procedure.

We can now move on to discuss the decay of neutral He using stochastic TD-CDFT, and for which a closed form of the KS single-particle quantum master equation cannot be obtained [6]. We prepare the system in such a way that both electrons (with spin σ) are in the first excited state of the ground-state Hamiltonian, $|\phi_\sigma(t=0)\rangle = |\epsilon_1\rangle$. This means that the Pauli exclusion principle is automatically satisfied by our environment operator (5). For this case we compare the stochastic evolution with the one in which $\hat{V} = 0$.⁴

In stochastic TD-CDFT both the ensemble-averaged density and current density are exact if we knew the exact functional. Approach to equilibrium could be thus monitored by discussing these two quantities. However, like in any other application of DFT, we take a step further and separate the density contributions into the different Kohn–Sham states. A direct physical meaning of these auxiliary states cannot be given, but they provide a convenient and intuitive way to interpret the results in terms of single-particle orbitals.

⁴ We use the local density approximation to the scalar exchange–correlation potential [2, 3], as derived by Ceperley and Alder [16] and parametrized by Perdew and Zunger [17]. The exchange–correlation vector potential is the one reported in [18], and we have used the interpolation formula in [19] for the electron viscosity.

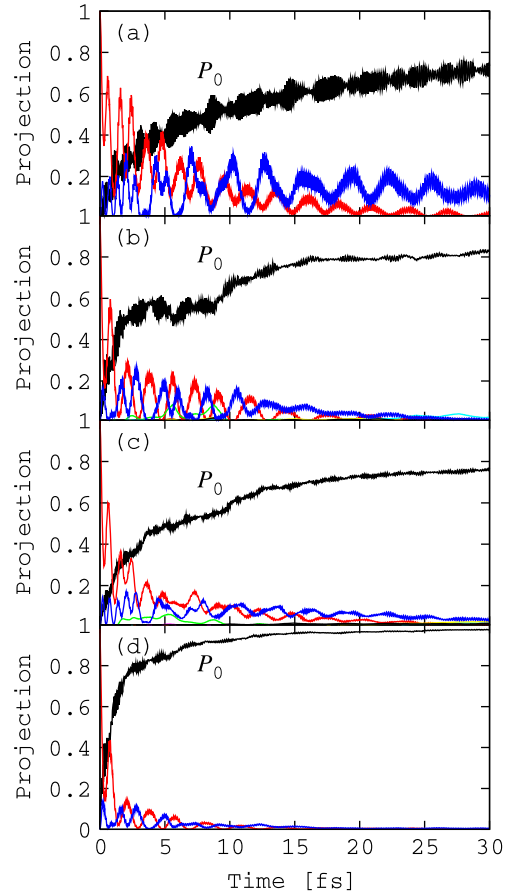


Figure 2. Panel (a): projections $P_i = |\langle \epsilon_i | \phi \rangle|^2$ for neutral He, as a function of time, for the case where the stochastic terms are not included (unitary evolution). The black, red (light gray), and blue (dark gray) curves correspond to P_0 , P_1 , and P_8 , respectively. Panel (b): same for as panel (a), but with the inclusion of the interaction with the environment. Panel (c): same for as panel (b), but averaged over five different runs, each with a different seed for the random number generator. Panel (d): same as for panels (a)–(c), except the dynamics were calculated using the wavepacket collapse methodology of equation (7).

In figure (2), we plot the projections $P_i = |\langle \epsilon_i | \phi \rangle|^2$ for the unitary evolution (panel (a)), as well as the projections for the non-unitary evolution for one realization of $\ell(t)$ (panel (b)) and averaged over five different realizations of $\ell(t)$ (panel (c)). As expected, in the presence of the environment, the projection onto the ground state $|\epsilon_0\rangle$ approaches 1, while the occupations of other states are suppressed as time goes on. Here, however, we also note another effect of the interaction. Figure 2(a) illustrates that, in the unitary evolution the projections P_i oscillate in time, which implies oscillations of the density, and are thus physically relevant. This oscillatory behavior reflects the motion of the electrons as they alternately fall toward the nucleus, and then rebound outward⁵. Interaction with the environment has the effect of not only dampening these oscillations⁶ but also of modifying their frequency, the

⁵ Sugino *et al* report similar high-frequency oscillations while studying the dipole moment of an isolated aluminum dimer [20].

⁶ Since we are using an approximate exchange–correlation vector potential with an effective viscosity, the internal electron friction also contributes to the dampening of these oscillations.

details of which vary depending on the particular realization of $\ell(t)$. The physical reason for this is that the introduction of the bath mediates new intermediate transitions for the single-particle wavefunction $|\phi\rangle$, thus effectively reducing the overall frequency of the oscillations.

We now discuss these results in terms of measurement theory. It is well-known that it is possible to interpret the interaction with an environment as a continuous ‘measurement’ of the state of the system—or, equivalently, of the state of the environment—with consequent non-unitary wavepacket reduction [21, 22]. We can make this point even clearer by assuming that every time the system interacts with the environment it emits a boson excitation (whether a photon or a phonon) and thus there is a finite probability $dp = dt|\langle\epsilon_1|\phi\rangle|^2/t_d$ that the emitted excitation be detected by an apparatus [23]. Upon detection of this excitation, the wavefunction $|\phi\rangle$ collapses to the ground state $|\epsilon_0\rangle$. This is the well-known postulate of wavepacket reduction.

We can write the above in the form of a Schrödinger-type equation of motion that includes a stochastic variable $\gamma(t)$, which has a probability distribution uniformly distributed between 0 and 1. If $\gamma > dp$, an emitted excitation is not detected, while if $\gamma < dp$, the emitted excitation is detected, and the wavefunction collapses to the ground state. That is, during a small time Δt , $|\phi\rangle$ evolves according to

$$|\phi(t + \Delta t)\rangle = \mu e^{-iH\Delta t} \theta(\gamma(t) - dp) |\phi(t)\rangle + \theta(dp - \gamma(t)) |\epsilon_0\rangle, \quad (7)$$

where $\theta(x)$ is the Heaviside step function, $H = H_{KS} - iV^\dagger V/2\tau$, and μ is the normalization factor⁷. A similar approach has been used by Dalibard *et al* in the context of quantum optics [23]. In the present problem, the term $iV^\dagger V/2\tau$ does not contribute much to the dynamics, but it is generally important since it represents a ‘null-measurement’ result in which no excitation has been emitted.

In figure 2(d) we plot the results from the time evolution of equation (7) for the problem of He relaxation. Starting with $|\phi(t = 0)\rangle = |\epsilon_1\rangle$, we evolved equation (7) in time for 1000 different realizations of $\gamma(t)$, and found the average value of $|\langle\epsilon_i|\phi(t)\rangle|^2$, which we have denoted by P_i . Note that each individual wavefunction starts in the excited state, and then suddenly drops to the ground state the first time that $\gamma(t) < dp$. This wavepacket reduction occurs at a different time for each run, and the ‘remaining’ excited states become exponentially less likely as time goes on; therefore, the average curve approaches an exponential. By comparing figure 2(d) with 2(c) we see that the non-unitary wavepacket reduction evolution is qualitatively similar to that provided by the stochastic Schrödinger equation (4). This equivalence therefore illustrates a point of contact between the stochastic Schrödinger equation (4) and quantum measurement theory: the environment ‘measures’ the state of the system, and, as a result, the wavefunction is modified in a non-unitary way. We observe, however, an important difference. In the wavepacket reduction formalism described

by equation (7), after the apparatus ‘detects’ the excitation, the system immediately collapses onto the ground state $|\epsilon_0\rangle$, *irrespective* of the interactions of the other states with the environment. In contrast, the non-unitary evolution of the stochastic Schrödinger equation (6) involves a constant process of *self-consistent* interaction with the bath. This implies that the frequency of small oscillations is unchanged in the wavepacket reduction formalism, while they change in time during dynamical interaction with the environment as described by equation (6). Clearly, one could introduce this effect into equation (7), but at a non-trivial complexity cost, while the stochastic Schrödinger equation (6) contains it naturally.

In summary, we have used stochastic TD-CDFT to describe the interaction of an excited quantum system (He) with an external environment, and its consequent decay into the ground state; a problem previously inaccessible via standard DFT methods. We have made a connection of this open quantum problem with quantum measurement theory thus showing that stochastic TD-CDFT may find applications in quantum information theory of realistic systems.

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⁷ It can be shown [23] that by defining an operator \hat{S} such that $\hat{S}|\epsilon_1\rangle = |\epsilon_0\rangle$, the density matrix $\hat{\rho}$ associated with equation (7) satisfies the Lindblad equation (6) with \hat{S} replacing \hat{V} .