Autoionizing Resonances in Time-Dependent Density Functional Theory

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Autoionizing resonances that arise from the interaction of a bound single-excitation with the continuum can be accurately captured with the presently used approximations in time-dependent density functional theory (TDDFT), but those arising from a bound double excitation cannot. In the former case, we explain how an adiabatic kernel, which has no frequency-dependence, can yet generate the strongly frequency-dependent resonant structures in the interacting response function, not present in the Kohn-Sham response function. In the case of the bound double-excitation, we explain that a strongly frequency-dependent kernel is needed, and derive one for the vicinity of a resonance of the latter type, as an \textit{a posteriori} correction to the usual adiabatic approximations in TDDFT. Our approximation is based on a Fano analysis of configuration mixing, and becomes exact for an isolated resonance in the limit of weak interaction, where one discrete state interacts with one continuum. We derive a “Fano TDDFT kernel” that reproduces the Fano lineshape within the TDDFT formalism, and also a dressed kernel, that operates on top of an adiabatic approximation.

We illustrate our results on a simple model system.

I. INTRODUCTION

The study of photoionization dates back to the beginning of quantum mechanics, with the photoelectric effect that was instrumental in establishing the particle nature of light. The threshold frequency at which ionization occurs is a characteristic property of the material under consideration. Today photoionization is still an important tool in characterizing the electronic structure of molecules, and it is desirable for theoretical methods to supplement, support, interpret, and even predict the experimental spectrum. Resonance structures, arising from the interplay of bound and continuum excitations (where this classification refers to some zeroth order model), create a fascinating panorama of peaks in the spectrum, whose profiles contain much information about the electronic states. For the theoretical description, one needs an accurate calculation of the continuum (unbound) states of the system. There are three major issues to be surmounted in treating resonances: first, resonances require an adequate treatment of electron correlation. We shall return to this point shortly, but note first that the considerable advances in electronic structure methods and codes for excitations over the years are predominantly set up for bound states, not continuum states: herein lies the second issue which is adapting the many-body methods for non-square-integrable scattering-type states\cite{1,2}. Both basis set issues as well as the finite matrix-based algorithms established in quantum chemistry codes need to be revisited. When the system of interest is a molecule rather than an atom, a third ingredient compounds the problem: treating the correlated continuum states in multi-center non-spherical potentials. A variety of theoretical methods have been developed to treat these issues to a variety of extents, and we mention only a smattering of these here. For atoms, one of the more successful approaches is multi-configuration Hartree-Fock\cite{3}. This has been shown to account for electron correlation and core polarization accurately enough to describe resonances in atoms well, as demonstrated in, for example, halogen atoms\cite{4}. For molecules, Ref.\cite{5} studied the relationship between interatomic distances and resonance positions using a minimal-basis static exchange method. Another approach utilizes R-matrix theory within multi-channel quantum defect theory, as for example in Ref.\cite{6}, for the case of the calcium atom. Reformulating the scattering problem as a bound-state problem in this way means that advanced electronic structure codes may be used. A complex-scaled full-configuration-interaction method was used in Ref.\cite{7} to calculate the resonances in a two-electron quantum dot. Methods using a complex absorbing potential in a configuration-interaction calculation, or with a correlated independent particle potential have been developed; an inner-valence autoionizing resonance of the neon-dimer Ne$_2^+$\cite{8}, the nitrogen dimer N$_2$ and acetylene C$_2$H$_2$\cite{9}, for example, were computed in this way. Several other works studied autoionizing resonances in acetylene, e.g. Ref.\cite{10} used configuration interaction within the multichannel Schwinger variational method, and Ref.\cite{11} used $L^2$ Gaussian-type orbital basis sets.

Accounting for electron correlation becomes an increasingly Herculean task for wavefunction-based methods as the number of electrons in the system grows. Time-dependent density functional theory (TDDFT) is a particularly efficient approach to the many-body problem, that makes it attractive for calculating photoionization spectra of chemically interesting systems. Re-
cent work by Stener, Decleva, Fronzoni, and co-workers, Refs. [12, 13, 14, 15, 16, 17] (and references therein), has shown that TDDFT predicts accurate resonance parameters for a range of medium-size molecules, including acetylene, carbon monoxide, silicon tetrafluoride, and sulphur hexafluoride. Their earlier work used a one-center expansion B-spline basis set, while the later ones utilized multi-centric B-spline basis functions, more suited to larger molecules.

TDDFT [18, 19, 20] is a time-dependent extension of the much older ground-state density functional theory, that operates by mapping the true system of interacting electrons, into one of non-interacting Kohn-Sham (KS) fermions that reproduces the exact time-dependent one-body density of the interacting system. The Runge-Gross theorem [18] proves that any property of the interacting system can be extracted, in principle, as a functional of just the time-dependent density and initial-state, and therefore from the time-dependent KS orbitals. Formally an exact theory, in practise approximations are required for the exchange-correlation contribution to the potential in which the KS electrons live, as a functional of the density and initial state, and also for extracting observables of interest from the KS system. As solving for the KS system is much faster than solving for interacting electrons, while still yielding properties of the true system, TDDFT enables the calculation of dynamics, excitations and response properties of molecules much larger than possible using traditional wavefunction methods. Its accuracy in the linear response regime [21, 22], for the calculation of response properties and spectra, is comparable to that of CASPT2 while its numerical efficiency compares with that of TDHF or even better [23, 24]; thus TDDFT has become a method of choice in quantum chemistry, especially for the calculation of bound spectra. One can now, for example, calculate spectra of systems as large as biomolecules (see eg. Refs. [25, 26, 27]), and run coupled electron-ion dynamics on non-trivial chemical reactions [28].

The KS spectrum is the response of the non-interacting KS system: single-particle excitations and oscillator strengths of the ground-state KS potential are computed. The spectrum of the true interacting system is obtained by applying the linear response TDDFT exchange-correlation kernel (see also Sec. III): operating via a matrix equation or a Dyson-type integral equation, the kernel mixes the single-excitations of the KS system, and, were the exact kernel known, this mixing would result in the exact spectrum of the true interacting system. The exact kernel is however unknown, and in practise, approximations are needed for it, as well as for the ground-state KS potential out of which the KS spectrum is calculated. Of particular note for the present paper, is that almost all calculations use an adiabatic approximation to the kernel, meaning one that has no frequency-dependence.

In the TDDFT calculations of auto-ionization cited above, the role of the channel coupling is very clear: the bare KS spectra are smooth and relatively featureless, while after the TDDFT procedure is applied, resonances are generated. In one of these earliest TDDFT calculations (in the Ne atom [12]), it was noted that while the resonances arising from bound single KS excitations whose energy lie in the continuum (eg. core to Rydberg excitations) are quite accurately predicted, those arising from bound double-excitations, are totally missed. (This was also noted to occur in acetylene [14]). This was explained in Ref. [12] as arising because the linear response method involves only first-order changes in the density (or wavefunction), and therefore only single-excitations can be obtained. However, in principle, TDDFT linear response reproduces all excitations of the system, which may be linear combinations of Slater determinants with any number of excited electrons. The lack of resonances from double-excitations is not a failing of TDDFT, but rather is a failing of the approximation for the exchange-correlation kernel that is used. The exchange-correlation kernel plays a crucial role, not only in mixing the single excitations of the KS system but also folding in its multiple excitations. For bound double-excitations, Ref. [29] showed that the usual adiabatic approximations to the TDDFT exchange-correlation kernel fail to fold in the multiple excitations, and that the exact kernel is necessarily strongly-frequency-dependent in the neighbourhood of a state of double-excitation character. An approximate frequency-dependent kernel was derived there to account for double-excitations; this was successfully tested on real molecules in Refs. [30, 31].

In the present paper, we investigate the form of the kernel that is needed in order to capture autoionizing resonances arising from a bound double-excitation with energy lying above the ionization threshold. Our derivation essentially adapts Fano’s 1961 analysis [32] to the case when the “unperturbed” states in his configuration-mixing are the relevant KS bound-state and the continuum its energy lies in. We begin therefore, in the next section, Sec. II with a brief recapitulation of Fano’s formula. In section III we discuss the implications of Fano’s formula for the density-density response functions of TDDFT, explaining with an illustrative sketch, that while a strong frequency-dependence is required in the TDDFT kernel to capture resonances arising from a bound double-excitation, resonances arising from bound single excitations can be captured by the usual adiabatic (non-frequency-dependent) TDDFT kernels. Then in section IV, we derive an approximation, in the spirit of Fano, which does capture the double-excitation resonance, and illustrate it on a simple model system. Our approximation becomes exact in the limit of weak interaction, for an isolated narrow resonance in a single continuum.

II. FANO RESONANCES

The universality of the Fano profile has been noted by many, from lineshapes in spectra of atoms, molecules,
solids and heterostructures, to interference in quantum dots and Aharonov-Bohm rings; its robustness reflected in the more than 3000 citations of his 1961 paper, Ref. 32. We consider here only the simplest type of resonance: when a single bound-state interacts with a single continuum. In the absence of this interaction, the continuum is assumed to be relatively “flat”, i.e. featureless. Fano performed a careful diagonalization of the Hamiltonian for a continuum coupled to a single bound state \( |\Phi_b\rangle \) whose energy lies in the continuum \( |\Phi_c\rangle \). The continuum states are assumed to be “pre-diagonalized”, that is, the zeroth-order (uncoupled) system accounts for the resonant coupling. Denoting the coupling Hamiltonian by \( V_{cpl} \), one defines the matrix element, \( V_E = \langle \Phi_E | V_{cpl} | \Phi_b \rangle \), with \( \Phi_E \) being the (uncoupled) continuum state. Fano derived the following result from the diagonalization:

\[
\frac{|\langle \Psi_E | \hat{T} | i \rangle|^2}{|\langle \Phi_E | \hat{T} | i \rangle|^2} = \frac{(q + \epsilon)^2}{1 + \epsilon^2} \tag{1}
\]

where \( \epsilon = E - E_r \) is a dimensionless energy:

\[
\epsilon = \frac{E - E_r}{\Gamma/2} \tag{2}
\]

defines the width of the resonance, while the parameter \( q \) characterizes its asymmetry:

\[
q = \frac{\langle \Phi_b | \hat{T} | i \rangle + P \int V_E |\langle \Phi_E | \hat{T} | i \rangle|/(E - E')dE'}{\pi V_E |\langle \Phi_E | \hat{T} | i \rangle|^2} \tag{3}
\]

For example, \( q = 0 \) represents a negative purely symmetric Lorentzian, \( q \to \infty \) represents a positive purely symmetric Lorentzian, and \( q = \pm 1 \) represents a purely antisymmetric lineshape. (See also later Fig. 11). The asymmetry can be interpreted as a consequence of interference between the autoionizing state and the continuum states \( 32, 33, 34 \). In Refs. 32, 33, it is argued that typically \( q \) is negative.

Although Eqs. 3 and 11 appear energy-dependent, \( q, \Gamma \), and also \( F(E) \) are regarded as constant through the resonance region. For a narrow enough resonance, this is a reasonable assumption; essentially the idea is that \( \Gamma \) is the smallest energy scale in the system. Fano also derived a “sum-rule” for the integrated transition probability:

\[
|\langle \Phi_b | \hat{T} | i \rangle|^2 = \int dE \left( \left| \langle \Psi_E | \hat{T} | i \rangle \right|^2 - \left| \langle \Phi_E | \hat{T} | i \rangle \right|^2 \right) = \left| \langle \Phi_E | \hat{T} | i \rangle \right|^2 \frac{\pi}{2} (q^2 - 1) \Gamma \tag{5}
\]

which expresses the unitary nature of the diagonalization procedure. Eq. 5 is essentially a consequence of the following closure relation:

\[
\int |\Psi_E \rangle \langle \Psi_E | dE = \int |\Phi_E \rangle \langle \Phi_E | dE + |\Phi_b \rangle \langle \Phi_b | \tag{6}
\]

Fano’s Eq. 11 tells us that the transition to the continuum when a discrete state couples to the continuum, is equal to that without the coupling, multiplied by a (generally asymmetric) Lorentzian line-shape factor. In terms of frequency \( \omega = E - E_i \), the lineshape factor (Eq. 1) is

\[
\frac{(q + \epsilon)^2}{1 + \epsilon^2} = \frac{(\omega - \omega_r + \Gamma q/2)^2}{(\omega - \omega_r)^2 + (\Gamma/2)^2} \tag{7}
\]

where

\[
\omega_r = E_r - E_0 = E_b - E_0 + P \int \frac{|V_E|^2}{E - E'}dE' \tag{8}
\]

Atomic units are used throughout this paper.

Photoabsorption cross-sections measure the dipole transition probability (see Section III), so in Fano’s formula, Eq. 11 take \( \hat{T} \) to be the dipole operator. Fits are routinely made for the Fano parameters \( q, \Gamma \), and \( \omega_r \), for a given cross-section obtained from experiment or theory, i.e. Eqs. 34 and 8 are not typically used to calculate these quantities, rather, they are extracted from experimental or theoretical data. Although we will only use this simplest form in the present paper, we do note that Fano’s analysis has been generalized in several directions 32, 34, 36, e.g.

\[
\sigma(\omega) = \sigma_1(\omega) \left( \frac{(\omega - \omega_r + \Gamma q/2)^2}{(\omega - \omega_r)^2 + (\Gamma/2)^2} \right) + \sigma_2(\omega) \tag{9}
\]

where there are two continua in the uncoupled case, \( \sigma_1(\omega) \) represents the contribution from a continuum that does(not) interact with the discrete autoionizing state. As one considers the more complicated situations, more fitting parameters are involved, and in practise fits are made for the more generalized formule, rather than the simplest situation discussed above.

III. AUTOIONIZING RESONANCES WITHIN ADIABATIC TDDFT

In this section we first briefly review the formalism for a photoionization/absorption calculation, with a view to its computation in TDDFT. Then we discuss how autoionizing resonances are described in adiabatic TDDFT; after deriving the Fano-equivalent formulæ for the TDDFT response functions.

A. Photoabsorption/ionization in TDDFT

In photoabsorption or photoionization, one essentially measures the transition dipole moments of the system
induced by an externally applied field (see eg. Ref. [35]). First, let us define the (complex) polarization:

$$\mathbf{P}(\omega) = \int \mathbf{r} \delta n(\mathbf{r}, \omega) d^3r$$  \hspace{1cm} (10)

The linear density response $\delta n(\mathbf{r}, \omega)$ may be written as

$$\delta n(\mathbf{r}, \omega) = \int \chi(\mathbf{n}_0)(\mathbf{r}, \mathbf{r}', \omega) \delta v_{\text{ext}}(\mathbf{r}', \omega) d^3r'$$  \hspace{1cm} (11)

where $\chi(\mathbf{r}, \mathbf{r}', t-t') = \delta n(\mathbf{r}, t)/\delta v_{\text{ext}}(\mathbf{r}', t)$ is the density-density response function of a system initially in its ground-state density $\mathbf{n}_0$, and $\delta v_{\text{ext}}(\mathbf{r}', t) = \mathbf{r}' \cdot \mathbf{E}(\omega)$ for an applied uniform field $\mathbf{E}$. Defining the polarizability tensor,

$$\alpha_{\alpha\beta}(\omega) = \int d^3r d^3r' r_\alpha r'_\beta \chi(\mathbf{r}, \mathbf{r}'\omega),$$  \hspace{1cm} (12)

(\alpha, \beta \text{ each run from 1 to 3 and denote the 3 spatial directions}), then $P_\alpha(\omega) = \sum_\beta \alpha_{\alpha\beta}(\omega) E_\beta(\omega)$. The photoabsorption or photoionization cross-section is then defined via

$$\sigma_{\alpha\beta}(\omega) = \frac{4\pi\omega}{c} \int_0^\infty m \alpha_{\alpha\beta}(\omega)$$

$$= \frac{4\pi\omega}{c} \int d^3r d^3r' r_\alpha r'_\beta Im \chi(\mathbf{r}, \mathbf{r}'\omega)$$  \hspace{1cm} (13)

An alternative sum-over-states expression may be obtained using the standard linear response theory expansion for the density-density response function (see eg. Ref. [36]):

$$\chi(\mathbf{r}, \mathbf{r}'\omega) = \sum_E \frac{\langle 0|\hat{n}(\mathbf{r})|E\rangle \langle E|\hat{n}(\mathbf{r}')|0 \rangle}{\omega - (E - E_0) + i0^+} \frac{\langle 0|\hat{n}(\mathbf{r}')|E\rangle \langle E|\hat{n}(\mathbf{r})|0 \rangle}{\omega + (E - E_0) + i0^+}$$  \hspace{1cm} (14)

where $|E\rangle$ label the excited states, and $|0\rangle$ is the ground-state with energy $E_0$, $\hat{n}(\mathbf{r}) = \sum_i \delta(\mathbf{r} - \mathbf{r}_i)$ is the density operator. Using the formula

$$\lim_{\nu \rightarrow 0} \frac{1}{\omega + i\nu} = P\left(\frac{1}{\omega}\right) - i\pi \delta(\omega)$$  \hspace{1cm} (15)

where $P()$ denotes the principal-value, and assuming real eigenstates, the imaginary part of the response function is extracted as

$$\Im \chi(\mathbf{r}, \mathbf{r}', \omega) = -\pi \sum_E \frac{\langle 0|\hat{n}(\mathbf{r})|E\rangle \langle E|\hat{n}(\mathbf{r}')|0 \rangle}{\delta(\omega - \omega_E) - \delta(\omega + \omega_E)}$$  \hspace{1cm} (16)

where $\omega_E = E - E_0$. Inserting this into Eq. (13) we have

$$\sigma_{\alpha\beta}(\omega) = -\frac{4\pi^2\omega}{c} \sum_E \frac{\langle 0|\hat{r}_\alpha|E\rangle \langle E|\hat{r}'_\beta|0 \rangle}{\delta(\omega - \omega_E) - \delta(\omega + \omega_E)}$$

$$= -\frac{4\pi^2\omega}{c} \sum_E d_\alpha(\omega) d_\beta(\omega) (\delta(\omega - \omega_E) - \delta(\omega + \omega_E))$$

where $d_\alpha(\omega)$ is the transition dipole moment from the ground-state to the excited state of energy $E = \omega + E_0$.

Therefore, to compute photoabsorption or photoionization, one needs an efficient way to calculate either the density response $\delta n(\mathbf{r}, \omega)$, or the density-density response function, $\chi(\mathbf{r}, \mathbf{r}', \omega)$ (Eq. (13)) or the excited states of the system (Eq. (17)). Given that the electrons in the system are interacting with all the others via Coulomb repulsion, this becomes a daunting task for correlated wavefunction methods for all but the smallest molecules: the numerical effort in solving the problem scales exponentially with the number of electrons in the system.

1. TDDFT

An alternative to wavefunction methods, which scales most favorably with system size, is TDDFT [18, 19, 20]. The interacting system, whose Hamiltonian is the sum of the kinetic energy operator $\hat{T}$, the electron-electron Coulomb repulsion $V_{\text{ee}}$ and the external potential (eg. nuclear attraction, plus a laser field) $V_{\text{ext}}(t)$,

$$\hat{H} = \hat{T} + V_{\text{ee}} + V_{\text{ext}}(t),$$  \hspace{1cm} (18)

is mapped onto a non-interacting, KS, system with a one-body Hamiltonian,

$$\hat{H}_S = \hat{T} + \hat{V}_S, \quad v_{\text{KS}}(\mathbf{r}, t) = v_{\text{ext}}(\mathbf{r}, t) + v_{\text{nuc}}(\mathbf{r}, t) + v_{\text{xc}}(\mathbf{r}, t).$$  \hspace{1cm} (19)

This is defined such that it reproduces the time-dependent density of the true system, $n(\mathbf{r}, t) = N \int d^3r_v d^3r_N |\Psi(\mathbf{r}, \mathbf{r}_2...\mathbf{r}_N)|^2 = \sum_{i=1}^N |\phi_i(\mathbf{r}, t)|^2$. In Eq. (19), $v_{\text{KS}}(\mathbf{r}, t) = \int n(\mathbf{r}', t)/|\mathbf{r} - \mathbf{r}'|$, and $v_{\text{xc}}(\mathbf{r}, t)$ is the exchange-correlation potential, a functional of the time-dependent density and initial true and KS states. Instead of dealing with the correlated many-body wavefunction, one solves for much simpler single-particle orbitals $\phi_i(\mathbf{r}, t)$ that evolve in the KS Hamiltonian Eq. (19), which nevertheless contain, in principle, not only correlation information of the true system, but all properties of the true interacting system may be extracted from them [18].

Linear response TDDFT is founded on the relation between the interacting and KS density-response functions, both of which are functionals of the ground-state density of the system of interest, $n_0(\mathbf{r})$. First, we note that for non-interacting systems such as the KS system, the numerator in Eq. (14) simplifies to products of occupied (indexed by $i$) and unoccupied (indexed by $a$) orbitals:

$$\chi_0[n_0](\mathbf{r}, \mathbf{r}', \omega) = \sum_{i,a} \left( \frac{\phi^*_i(\mathbf{r})\phi_a(\mathbf{r})\phi^*_a(\mathbf{r}')\phi_i(\mathbf{r}')}{\omega - (\epsilon_a - \epsilon_i) + i0^+} \right.$$  \hspace{1cm} (20)

$$- \frac{\phi^*_i(\mathbf{r})\phi_a(\mathbf{r})\phi^*_a(\mathbf{r}')\phi_i(\mathbf{r}')}{\omega + (\epsilon_a - \epsilon_i) + i0^+} \right)$$

The orbital energy-differences in the denominator ($\epsilon_a - \epsilon_i$) are the KS single-excitation excitations. These are not
the frequencies of the true system, which lie at the poles of the true interacting response function, $\chi(r, r', \omega)$. This is obtained by the Dyson-like equation:

$$\chi[n_0](r, r', \omega) = \chi_S[n_0](r, r', \omega) + \int dr_1 dr_2 \chi_S[n_0](r_1, r_1, \omega) f_{\text{hxc}}[n_0](r_1, r_2, \omega) \chi[n_0](r_2, r', \omega)$$

where $f_{\text{hxc}}$ denotes the “Hartree-exchange-correlation kernel”

$$f_{\text{hxc}}[n_0](r, r', \omega) = \frac{1}{|r-r'|} + f_{xc}[n_0](r, r', \omega)$$

with

$$f_{xc}[n_0](r, r', t-t') = \frac{\delta v_{xc}[n](r, t)}{\delta n(r', t)}$$

Although the exact $xc$ kernel, $f_{xc}(\omega)$ is frequency-dependent, reflecting a dependence on the history of the density in the time-domain, the majority of calculations today utilize an “adiabatic” approximation, meaning one where $v_{xc}[n](r, t)$ depends only on the instantaneous density $f_{xc}[n_0](r, r', t-t') \propto \delta(t - t')$. When Fourier-transformed, this gives no structure in frequency-space. Instead, the adiabatic approximation is based on a ground-state energy functional:

$$f_{xc}^0[n_0](r, r') = \frac{\delta^2 E_{xc}[n](r)}{\delta n(r')^2} |_{n=n_0}$$

Despite incorrectly lacking frequency-dependence, the adiabatic approximation yields remarkably accurate results for most excitations. In most quantum chemistry codes, where one is interested in calculating excitation energies and oscillator strengths of bound states in finite systems, Eq. (21) with an adiabatic approximation for $f_{xc}$ is transformed to a matrix equation indexed by KS single-excitations. The matrix effectively mixes the single excitations of the KS system, and when the true interacting state is composed of mixtures of KS single excitations, adiabatic TDDFT is expected to work reasonably well – provided the spatial functional dependence of the xc potential is adequately nonlocal for the problem at hand. (For example, one needs to go beyond the semi-local GGA’s to capture excitation energies for high-lying Rydberg states, although see also $^{39}$), or long-range charge-transfer excitations $^{40, 41}$, or polarizabilities of long-chain molecules $^{42, 43, 44}$). For states of multiple-excitation character however, one must go beyond the adiabatic approximation as was shown for bound states of finite systems $^{23, 30, 31, 43, 44}$, as mentioned in the introduction. We shall show shortly, that also when such a state lies in the continuum, a frequency-independent kernel totally misses the resonance arising from it.

B. Autoionizing Resonances in TDDFT

In photo-ionization, the energy of interest lies in the continuum; the sum over the delta-function peaks in Eqs. (10) and (17) becomes an integral, and, (for positive $\omega$, greater than the ionization threshold),

$$\Im \chi(r, r', \omega) = -\pi \langle 0 | n(r) | E = \omega + E_0 \rangle \langle E = \omega + E_0 | n(r') \rangle|0 \rangle$$

where the continuum states are chosen real and energy-normalized. The bare KS cross-section for transitions to the continuum are largely structureless, especially when only one continuum is relevant:

$$d_{\omega} = \langle \phi_{\epsilon=\epsilon+i\omega} | r | \phi_i \rangle$$

where $\phi_i$ is the KS occupied orbital, of energy $\epsilon_i$, out of which excitation occurs to the continuum orbital $\phi_\omega$, of energy $\epsilon_i = \epsilon + \omega$. These oscillator strengths typically gently decay as a function of frequency, reflecting the decay of the overlap between an occupied orbital and a continuum one as the energy of the continuum state rises. In the case of overlapping continua, at frequencies in which a new ionization channel becomes accessible, the spectrum displays an “absorption jump” $^{34}$ but these are often hidden by the autoionization Rydberg series preceding it.

When one applies TDDFT to obtain the spectrum of the interacting system, the kernel $f_{\text{hxc}}$ mixes the KS single excitations and the spectrum distorts to varying degrees: less at the higher frequencies, and most significantly near resonances. The TDDFT kernel smears the oscillator strength from bound transitions whose energy lies in the continuum over a narrow range in the continuum, implicitly performing the job of the Fano diagonalization of Section 11. Effectively, a rather featureless KS continuum spectrum is turned into a dramatically frequency-dependent interacting spectrum, via the operation of the xc kernel. Refs. $^{12, 13, 14, 15, 16, 17}$ have demonstrated this explicitly on a wide range of interesting atoms and molecules. These works show that adiabatic kernels reproduce resonance features of interacting systems rather well through this action, when the resonances arise from a bound single excitation with energy lying in the continuum (e.g. of core-Rydberg nature).

The appearance of the resonance can therefore be understood as a mixing of the single excitations appearing in Eq. (20) via Eq. (21). Yet, how a frequency-independent kernel can transform the largely frequency-independent KS continuum spectrum into a spectrum that does have such dramatic frequency-dependence, may strike one as incongruous. To understand this better, we first find an expression relating the interacting and KS response functions near an autoionizing resonance, following in Fano’s footsteps.

We keep to the simple case of one discrete state lying in one continuum. Further, we consider, initially, only the resonant coupling; that is, we treat the KS states as Fano’s “pre-diagonalized” states, without accounting for mixing amongst them. Although this could only be the case when there is no electron-interaction, the justification for this simplification is that in the vicinity of the resonance, this resonant coupling is certainly the dominant
effect: the coupling amongst the KS states is an order of \( \Gamma \) less. (Later, in Sec.\[\text{14}\] we relax this assumption). The matrix elements on the right-hand-side of Eq. (24) have a similar form to the matrix element in Eq. (1): taking \( T \) as the density operator \( \hat{n}(r) \), we have

\[
\langle 0 | \hat{n}(r) | E \rangle = \sqrt{\frac{(\omega - \omega_r + \Gamma q(r)/2)^2}{(\omega - \omega_r)^2 + (\Gamma/2)^2}} \langle 0 | \hat{n}(r) | E \rangle \ 
\]

where the ket on the right is the KS continuum excited state at energy \( E = \omega + E_0 \). The state \( |0\rangle \) on both sides of the equation is the initial state out of which transitions occur, which we will take to be the ground-state. Technically, this should be the interacting ground-state because Fano’s analysis assumed everything except for the resonant coupling was in the zero-order states. However, if we approximate the bra \( \langle 0 | \) on the right of Eq. (26) to be instead the KS ground-state, this formula then directly relates the interacting matrix element (related to the oscillator strength) to the KS matrix element. This approximation holds if the KS ground–continuum transition in the absence of the resonance is a good approximation. The quantities \( \Gamma, q, \omega_r \), have the forms as in Eqs. (3) and \( \text{8} \) where the “coupling” \( V_{\text{cpl}} \) is the difference in the Hamiltonian of the true and KS systems, i.e. from Eqs. (15) and (19).

\[
V_{\text{cpl}} = V_{ee} - v_{\text{XC}} \ 
\]

Inserting Eq. (26) into Eq. (24) for \( \omega \) near a resonance,

\[
\Im \chi(r, r', \omega) = \frac{(\omega - \omega_r + \Gamma q(r)/2)(\omega - \omega_r + \Gamma q(r')/2)}{(\omega - \omega_r)^2 + (\Gamma/2)^2}
\times \Im \chi^{c}(r, r', \omega) \ 
\]

where \( \chi^{c}(r, r', \omega) \) denotes the continuum contribution to the KS response function at frequency \( \omega \). Following directly from Fano’s analysis, Eq. (28) is a new relation between the true and KS response functions in the neighborhood of any isolated narrow autoionizing resonance, that arises from the mixing of a single discrete state with a single continuum, under the assumption of weak interaction.

For purposes of illustration, which will be useful shortly, we plot a representation of the response function and its inverse in Figure 1 for \( q \) fixed at \(-3\) (top panels), and at \( 1 \) (lower panels). One may consider \( r \) and \( r' \) as fixed in these figures (or integrated over, as in a calculation of the cross-section, Eq. (13)); we are interested here in the frequency-dependence of the response functions, not their spatial-dependence. For this reason, the plots of the inverse response functions in the right-hand panels must not be taken too literally. The KS response function is assumed to have a rather unremarkable frequency-dependence, gently decaying, as discussed earlier, and consistent with the “flat” unperturbed continuum assumption of Fano \([32, 34]\). (In the plots, we used simply \( \chi^{c}(\omega) \approx \frac{1}{\sqrt{\omega^{2} - \omega_{b}^{2}}} \), where the ionization potential \( I = 0.5a.u. \). The y-axes of the plots are in arbitrary units.)

We now return to the curiosity raised earlier regarding how application of a frequency-independent adiabatic kernel to the flat KS spectrum can generate frequency-dependent resonant structure in \( \chi \). A simple sketch is instructive to show this. Consider a resonance due to a bound single-excitation, at frequency \( \omega_{b} > I \) (\( I \) is the ionization potential). Within our weak-interaction assumption that the KS single excitation couples only to the continuum states, the KS response function near frequency \( \omega_{b} \) has the form

\[
\chi_{b}(\omega) = \chi^{c}_{b}(\omega) + \chi^{b}_{b}(\omega) \ 
\]

where \( \chi^{c}_{b}(\omega) \) is complex, smooth and gently-decaying and \( \chi^{b}_{b}(\omega) \) is the contribution of the bound state to the sum over states Eq. (20). Again, for present purposes, we neglect the spatial-dependence. We take \( \chi^{c}_{b}(\omega) \) with no dependency on this form, and \( \chi^{b}_{b}(\omega) = \frac{b}{\omega - \omega_{b} + i \Gamma_{b}} \). Here \( b \) represents the orbital products appearing in the residue of Eq. (20). The imaginary part of this \( \chi_{b}(\omega) \) is plotted as the solid line on the top left panel of Figure 1. In particular, note that \( \Im \chi^{c}_{b} \), which is directly related to the measured cross-section (Eq. (13)), has the structureless continuum contribution plus a delta-peak (indicated by the arrow) at \( \omega_{b} \) (taken to be 3, while \( b \) is taken to be 0.01 in these plots; other values yield similar plots). The delta-function peak that results from the pole when the imaginary part is taken (Eq. (13)) in obtaining the cross-section is not evident in the smooth KS cross-sections.

FIG. 1: The real and imaginary parts of \( \chi(\omega) \) for \( q = -3 \) (top left panel), and for \( q = 1 \) (lower left panel) as a function of frequency \( \omega \) (see text). The panels on the right show the corresponding inverse response functions. The width \( \Gamma \) is chosen to be 0.1 and resonance position \( \omega_{r} = 3 \).

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plotted in the graphs of Refs. [12, 13, 14, 15, 16, 17], because there only the KS continuum transitions in $\chi_S^{-1}$ (Eq. (25)) are included. Now we simply invert Eq. (29) and, interestingly, this immediately displays resonance-structures in both the real and imaginary part of $\chi_S^{-1}(\omega)$, as shown by the solid lines on the right-hand panel of Figure 2. This may be simply seen mathematically: inverting Eq. (29) reveals a Lorentizan denominator in both the real and imaginary parts. Applying the TDDFT kernel, to obtain $\chi^{-1} = \chi_S^{-1} - f_{\text{Hxc}}^A$ (Eq. (22)), we see that an adiabatic approximation $f_{\text{Hxc}}^A$ (Eq. (23)) just uniformly shifts the real part of $\chi_S^{-1}$, while not adding any additional frequency-dependence. Indeed the resonance structure of $\chi_S^{-1}$ and the adiabatically shifted one $(\chi_A^{-1})$ resemble that of the Fano profile displayed in Figure 1 (consider there the top right $q = -3$ panels); no frequency-dependence is required in the kernel itself to obtain resonances in $\chi_S$. We now invert $(\chi_A^{-1})$ to obtain $(\chi_A)$, plotted back in the left-hand panels of Figure 2. This resembles the top left Fano profile in Figure 1. The adiabatic shift in the inverse response functions, had the effect of Lorentzian smoothing the delta-function peak in $\Im \chi_S$, producing a resonance in $\Im \chi_A$. Therefore, making a adiabatic shift in the real part of the inverse response fn, $\Re \chi_S^{-1}$, turns, upon inversion, a delta-peak of $\Im \chi_S$ into a Lorentzian resonance peak of $\Re \chi_A$. In this way a frequency-independent shift of $\chi_S^{-1}$ generates frequency-dependent structure in $\chi$.

For a resonance arising from a double-excitation however, the analogous figures clearly show that frequency-dependence in the kernel is absolutely required. The KS response function of Eq. (29) now consists solely of the gently decaying first term, $\chi_S$, (left-hand panel of Figure 3) i.e. there is no bound-state contribution to $\chi_S$ because a double-excitation has zero oscillator strength [29]. The density-density response function involves matrix elements of the one-body density operator between the ground and excited states. For the KS system, these states are single Slater determinants; therefore, if the excited state differs from the ground state by more than one orbital, as in the case of a double-excitation, the matrix element gives zero. Put another way: linear response in the KS system can only excite one electron, whereas the true interacting states are mixtures of single and double and higher excitations, so have non-zero oscillator strength. On the right panel of Figure 3 we invert this smooth $\chi_S$ to obtain the featureless $\chi_S^{-1}$ shown (solid lines). A frequency-independent kernel again only shifts the real part of this uniformly as shown, but in this case it cannot generate the resonance-structure of the true $\chi^{-1}$ shown as dotted lines in the figure. For that, a frequency-dependent kernel of the form derived in the next section is required. The left-hand panel shows the real and imaginary parts of $\chi_S$ and $\chi_A$, lacking resonance.

![FIG. 2: The real and imaginary parts of $\chi_S(\omega)$ (left-hand panels, solid lines). The delta-function in the imaginary part of $\chi_S$ corresponding to the bound-state, is shown as an arrow. On the right panel, we show the real and imaginary parts of $\chi_S^{-1}$ (solid) and the shift that an adiabatic kernel $f_{\text{Hxc}}^A$ produces, yielding $(\chi_A^{-1})$ (dashed). When this is inverted to yield the adiabatic response kernel $\chi_A(\omega)$, the resonance emerges, as indicated by the dashed lines on the left panels. The adiabatic curves should be compared with the $q = -3$ panels of Fig. 1 - the adiabatic kernel is able to approximate the true resonance structure in this case.](image)

![FIG. 3: The real and imaginary parts of $\chi_S(\omega)$ (left-hand panels, solid lines). On the right panel, we show the real and imaginary parts of $\chi_S^{-1}$ (solid) and $(\chi_A^{-1})$ (dashed) that arises from application of an adiabatic kernel $f_{\text{Hxc}}^A$ as indicated. The dotted lines show the real and imaginary parts of the true inverse kernel $\chi_s^{-1}$ (as in the left-hand $q = 1$ panel of Fig. 1) - the adiabatic kernel completely misses the resonance in this case.](image)

In summary, for the case of an autoionizing resonance arising from a bound single-excitation, an adiabatic kernel, despite being frequency-independent, can nevertheless generate the strongly frequency-dependent resonant structure in the interacting response function, when applied to the largely frequency-independent Kohn-Sham response function. This works because an adiabatic kernel uniformly shifts the real part of the inverse response function; when inverted back, a Lorentzian form appears, and the adiabatic response function displays resonances.

In the next section we derive the xc kernel which can recapture the Fano resonance for the case of a bound double-excitation.
IV. DRESSED TDDFT FOR RESONANCES ARISING FROM DOUBLE EXCITATIONS

We are interested in the frequency-range near a resonance that arises when the energy of a bound double-excitation lies above the single-ionization threshold. As argued in the previous section, the KS response function displays no resonance, and an adiabatic kernel cannot generate one. In this section we derive the form of the kernel that is required in order to capture this kind of resonance, based on the analysis of Fano. We once again keep within the assumption of weak interaction, where the largest coupling between the KS states near the frequencies of interest, is the resonant coupling of the bound double-excitation with the continuum states. We again assume an isolated resonance: one discrete state coupling to one continuum.

Eq. 25 relates the imaginary part of the true response function to that of the KS response function via the Fano lineshape. Our job is now to use Eq. 22 to find the implied structure of the xc kernel.

A first simplification is that \( q^2 = 1 \). This follows from the sum-rule Eq. 5. Within the assumption that \(|i\) can be approximated by the KS ground-state, then the RHS must be zero, since \( \hat{T} \) is a one-body operator and \( \Phi_i \) differs from the KS ground-state by two orbitals. That \( q^2 = 1 \) is consistent with the oscillator strength sum-rule (eg. Ref. [33]): both the KS system and the interacting system satisfy the oscillator strength sum-rule. As the KS spectrum does not contain the resonance arising from a doubly-excited state, this suggests that the integrated area under the Fano lineshape factor should be zero. That is, the line-shape should be antisymmetric, so \( q(\mathbf{r}) \) should be \( \pm 1 \).

Examination of Eq 3 reveals that \( q \) must be positive for our case: the first term in the numerator on the right is zero by the above argument, while the second term divided by the denominator is positive [32], because \( \langle \Phi_i | \hat{T} | i \rangle \) grows larger than \( \langle \Phi_i | \hat{T} | i \rangle \) where \( E - E' > 0 \).

So we may conclude for the case of a double-excitation resonance, in the weak-interaction limit, that the imaginary part of the response function is given by:

\[
\Im(\omega) = \frac{(\omega - \omega_r + \Gamma/2)^2}{(\omega - \omega_r)^2 + (\Gamma/2)^2} \Im(\omega) \tag{30}
\]

where \( \Gamma \) and \( \omega_r \) are given by Eqs. (3) and (8), with \( V_{\text{cpl}} \) given by Eq. 27. An immediate implication is that the spatial-dependence is unchanged: this is true only within the approximations stated above.

Returning to our search for \( f_{\text{HXC}} \), Eq. 22 requires that we invert the response function. For this, we need to first calculate its real part, which we may obtain from the principle-value integral:

\[
\Re(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\omega' \Im(\omega')}{\omega^2 - \omega'^2} d\omega' \tag{31}
\]
due to known analyticity properties of \( \Im(\omega) \) (eg. Ref. [34]). Subtracting out \( \Im(\omega) \) from \( \Im(\omega) \), we write

\[
\Re(\omega) = \Re(\omega) + \frac{2\Gamma}{\pi} \int_0^\infty \frac{\omega' \Im(\omega')}{(\omega^2 - \omega'^2)((\omega - \omega_r)^2 + (\Gamma/2)^2)} d\omega' \tag{32}
\]

In the spirit of the Fano analysis, we assume that the KS orbitals are slowly-enough varying in frequency, that \( \Im(\omega) \) can be pulled out of the principle-value integral. That is, that \( \Im(\omega) \) is relatively flat in the region of the resonance; further away from the resonance the integral vanishes as the line-shape factor decays rapidly. We obtain

\[
\Re(\omega) = \Re(\omega) + \frac{\Gamma^2/2}{(\omega - \omega_r)^2 + (\Gamma/2)^2} \Im(\omega) \tag{33}
\]

Consistent with our assumptions, we take \( \Gamma << (\omega_r - \Gamma) \), and considering frequencies \( \omega \) near \( \omega_r \), we obtain, after some algebra,

\[
\Re(\omega) = \Re(\omega) + \frac{\Gamma^2/2}{(\omega - \omega_r)^2 + (\Gamma/2)^2} \Im(\omega) \tag{34}
\]

Corrections to this are \( O(\Gamma/\omega_r) \), so are neglected.

Putting Eqs. 34 and 30 together, we have

\[
\chi = \chi_0 + \frac{\Gamma(\Gamma/2 + i(\omega - \omega_r))}{(\omega - \omega_r)^2 + (\Gamma/2)^2} \Im(\omega) \tag{35}
\]

The complex lineshape on the right relates the interacting response function to the non-interacting one with a dramatic resonance structure. The cross-section obtained from the imaginary part, reproduces the Fano formula.

One should not be alarmed by the poles in the upper half plane, that our approximate \( \Im(\omega) \) possesses, given that the exact \( \chi \) should be analytic in the upper half plane, and its inverse \( \chi^{-1} \) analytic for \( \Im(\omega) > 0 \). But our approximate kernel holds only for real frequencies, moreover, for frequencies in the restricted range near the resonance.

We now use Eq. 22 to extract the frequency-dependent kernel. Subtracting the inverse of Eq. 35 from that of \( \chi_0^{-1} \) (Eq. 22) we find the Hartree-exchange-
correlation kernel to be
\[ f_{\text{HXC}}(\omega) = \chi_s^{-1} - \left( \chi_s + \frac{\Gamma/2 + i(\omega - \omega_r)}{(\omega - \omega_r)^2 + \left(\frac{\Gamma}{2}\right)^2} \chi_s \right)^{-1} \] (36)

We call this the “Fano TDDFT kernel”, in that it reproduces exactly the Fano lineshape when a bound double-excitation lies in the continuum. Its frequency-dependence is essential, as demonstrated by the sketches of the previous section. For illustration, we plot the real and imaginary parts of this in Figure 4 where we take \( \chi_s(\omega) \approx \frac{1}{\sqrt{\omega+1}} + \frac{1}{\sqrt{\omega-1}} \) as in the earlier plots, \( \Gamma = 0.1, \omega_r = 3 \).

This kernel accounts only for the coupling of the KS bound state to the continuum, which is the dominant effect near the resonance. It becomes exact in the limit of weak interaction, for an isolated and narrow resonance, where \( \Gamma \) is the smallest energy scale of the system.

We may also include this kernel on top of an adiabatic kernel, in order to account also for mixing of non-resonant single excitations that adiabatic TDDFT may capture well. For this to be practicable, we have to produce a kernel that is well-isolated from any other response. With this aim, we substitute Eq. 36 into the dressed response function leaves untampered the usual resonance (Eq. 35). Thus we also need to utilize Eq. 38 directly, instead we would use Eq. 39. Instead, Eq. 39 and Eq. 38 are of fundamental interest here; it is the adiabatic-correlation kernel that needs to be approximated in TDDFT, and these equations reveal the form it requires, in order to reproduce the Fano resonance arising from a double-excitation.

### A. Model example

We illustrate our results on a simple model involving two electrons in one-dimension living in an external potential of the form:

\[ v_{\text{ext}}(x) = -\frac{U_0}{\cosh^2(\alpha x)} - \beta \sqrt{1 - \tanh^2(x)}^3 \] (40)

We choose values of parameters \( U_0, \alpha, \beta \) such that there are (at least) two bound single-particle states in the non-interacting problem. A sketch is shown in Figure 5. A double-excitation to the first excited orbital is shown on the left; this has energy \( 2\epsilon \) where \( \epsilon \) is the energy difference between the single-particle orbitals. This energy \( 2\epsilon \) exceeds the single-ionization threshold for this system, and lies in the continuum; therefore the state on the left is degenerate with a single-excitation to the continuum, indicated on the right. When electron-interaction is turned on, an isolated resonance is created, of the type to which our formula and analysis applies.

We first find the KS potential and spectrum. We choose a weak delta-function interaction:

\[ V_{ee} = \lambda \delta(x - x') \ , \ \lambda < 1 \] (41)

For small enough \( \lambda \), exchange dominates over correlation. We use the exact-exchange approximation for two electrons:

\[ v_{\text{xc}} = -v_\text{HI}/2 = -\lambda \chi(x)/2 \] (42)

Eq. 19 then yields the KS potential:

\[ v_\text{xc}(x) = -\frac{U_0}{\cosh^2(\alpha x)} \] (43)
is smooth and gently decaying.

and dipole moment, shown as the dashed line in Fig-

orbitals we may calculate the KS response function

strength,

pute everything only to first-order in the interaction

be obtained with the Fano TDDFT kernel Eq. 36, and the

non-interacting bound orbital energies

states and energies of one-particle states: we chose

0

U

in many quantum mechanics textbooks. The parameters

0

are chosen such that there are at least two bound

one-electron orbitals. We may calculate the KS response function \( \chi^p \) and dipole moment, shown as the dashed line in Figure 6, after placing two electrons in the lowest orbital. Allowing the electrons to interact couples these degenerate states, creating a resonance.

if we take \( \beta = \lambda \) in Eq. 40. The exact one-electron eigenstates and energies of \( v_0 \) (an "Eckart well") can be found in many quantum mechanics textbooks. The parameters \( U_0, \alpha \) are chosen such that there are at least two bound one-particle states: we chose \( U_0 = 1.875 \), and \( \alpha = 1 \), which places the non-interacting bound orbital energies at \( \epsilon_0 = -1.125 \) and \( \epsilon_1 = -0.125 \). From the one-electron orbitals we may calculate the KS response function \( \chi^p \) and dipole moment, shown as the dashed line in Figure 6 after placing two electrons in the lowest orbital. As expected, the dipole moment to the continuum states is smooth and gently decaying.

\[
\chi^A(r, r', \omega) = \chi^p(r, r', \omega) + \frac{\lambda}{2} \int \chi^p(r, r_1, \omega) \chi(r_1, r', \omega) d^3r_1
\]

where, on the right, we may replace \( \chi \) with \( \chi^p \) to get the \( O(\lambda) \) adiabatic TDDFT spectrum. In one-dimension, from Eqs. 13 and 14

\[
|d(\omega)|^2 = -\frac{1}{\pi} \int x \Im \chi(x, x', \omega) dx dx'
\]

The KS version of Eq. 21 simplifies to

\[
\Im \chi^p(x, x', \omega) = -\pi \phi_0(x) \phi_0(x') \phi_{\epsilon = \omega + \epsilon_0}(x) \phi_{\epsilon = \omega + \epsilon_0}(x')
\]

Using Eq. 47 and its principal-value integral to get the real part, Eq. 49 finally gives

\[
|d^A(\omega)|^2 = |d_0(\omega)|^2 + 2\lambda d_0(\omega) \times \int dx_1 \phi_0^2(x_1) \phi_{\epsilon}(x_1) P \int d_0(\epsilon') \phi_{\epsilon'}(x_1) \frac{\epsilon' - \epsilon_0}{\epsilon^2 - (\epsilon' - \epsilon_0)^2} d\epsilon' d\epsilon
\]

This adiabatic dipole moment in Fig[6] as the dotted line: it smoothly shifts the KS spectrum, redistributing oscillator strength from the lower frequencies of the KS spectrum to higher frequencies, but is a small and smooth correction.

Applying now the frequency-dependent kernel Eq. 50 to compute the spectrum reveals the resonance; applying the dressed kernel Eq. 51 incorporates corrections from the adiabatic approximation as well as capturing the resonance. As mentioned in the previous section, in practice, we utilize Eq. 52 evaluating \( \Gamma \) and \( \omega_r \) using the KS orbitals.

V. CONCLUSIONS AND OUTLOOK

We have discussed the implications of Fano’s resonance lineshape formula for the exchange-correlation kernel of TDDFT. Within the limit of a narrow isolated resonance involving one discrete state and one continuum, and weak interaction, we derived the Fano-equivalent formula for the imaginary part of the TDDFT response function (Eq. 28). We illustrated how a frequency-independent kernel applied to a largely frequency-independent KS response function, actually yields dramatic frequency-dependent resonant structures for the case of a bound single-excitation, but yields no structure in the case of a bound double-excitation.
Within our assumptions, we derived the exact form of the frequency-dependent kernel that is needed for the latter case: we call this the Fano TDDFT kernel, in the sense that it exactly reproduces Fano's lineshapes, when applied to the KS density-response function. We then proposed a dressed frequency-dependent kernel, that accounts for the Fano effect on top of an adiabatic approximation. The form of these kernels is of fundamental interest for TDDFT. In practise, we propose one computes the resonance width $\Gamma$ and position $\omega_r$, using the appropriate KS orbitals; compose from them the Fano lineshape (Eq. (20)) and thereby modify the adiabatic spectrum. How this will work in practice for molecules of interest, remains to be tested.

In this paper we considered the simplest case of a resonance arising from a bound double excitation: that is, when the resonance is isolated from all others and only one continuum and one discrete state are involved. We have not considered the interaction of resonances \(^{[17]}\) that arises in most systems, nor the computation of individual branching ratios when several channels are involved \(^{[18]}\). The work in the present paper is only a first step in uncovering how the exact exchange-correlation kernel captures resonances in the general case, and how to approximate it in practice.

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