



Dynamical Reorganization of Two-Electron Correlation During Atomic Excitation and Relaxation A reduced-density-matrix framework for cascade pathways

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Abstract: Electron correlation is central to the structure and dynamics of two-electron atoms. Excitation and radiative relaxation are usually described through energies, state populations, and transition probabilities, while the associated reorganization of genuine two-electron correlation provides complementary information. We formulate a reduced-density-matrix framework for following this reorganization during excitation and subsequent radiative relaxation. The two-particle reduced density matrix (2-RDM) is separated into the contribution reconstructed from the one-particle density matrix and a cumulant part, and a reference-state correlation distance is introduced to quantify the displacement of the instantaneous correlation structure from that of a chosen reference state. An analytically tractable two-configuration model shows why populations alone cannot determine the full two-electron density matrix. The framework is then formulated for the helium cascade $1s3d\ ^1D_2 \rightarrow 1s2p\ ^1P_1^o \rightarrow 1s^2\ ^1S_0$. The purpose is not to introduce a new density matrix or a new cumulant measure, but to use established RDM quantities to define and test a correlation-space trajectory for an atomic relaxation pathway. No Cooper-like pairing assumption is made. The proposed quantities can be evaluated using time-dependent configuration interaction or time-dependent 2-RDM methods. The paper establishes a testable framework; no numerical correlation trajectory is claimed until a converged calculation is performed.

Keywords: electron correlation; two-particle reduced density matrix; cumulant; helium; configuration interaction; radiative cascade; atomic relaxation.

Introduction

The helium atom is the simplest neutral atom in which the electron–electron Coulomb interaction produces a genuinely correlated two-electron problem. High-accuracy treatments of helium have a long history, beginning with explicitly correlated Hylleraas wavefunctions and followed by increasingly accurate variational and configuration-interaction methods. These studies established both the importance of the interelectronic coordinate and the limitations of independent-particle descriptions.

For time-dependent processes the distinction between one-electron and two-electron information becomes especially important. Time-dependent natural orbitals and occupation numbers can change substantially during atomic excitation. Electron-pair densities have also been used to follow exchange and Coulomb correlation during time-dependent helium dynamics. More generally, time-dependent two-particle reduced-density-matrix (TD-2RDM) methods have been developed for correlated many-electron dynamics and nonlinear atomic response. Experimentally, correlated two-electron wave-packet dynamics in helium have been reconstructed using attosecond transient-absorption spectroscopy.

The 2-RDM is an established many-body quantity, and the cumulant part of the 2-RDM has previously been proposed as a quantitative measure of electron correlation. Correlation analyses based on the cumulant have also been used to distinguish dynamic and nondynamic contributions. Thus neither the 2-RDM nor the cumulant is claimed to be new here.

The narrower question addressed in this paper is instead:



Does atomic relaxation follow a characteristic trajectory in two – electron correlation space?

A related question is whether relaxation retraces the correlation trajectory generated during excitation. There is no general reason to assume such retracing. Excitation and radiative decay occur under different dynamical conditions and may involve different intermediate states.

The proposed contribution is therefore a reference-state correlation-distance functional constructed from established RDM quantities. Its purpose is to compare the instantaneous correlation structure with that of a chosen reference state and to follow the resulting trajectory through an excitation–cascade–relaxation process.

Literature context and research gap

The present framework is deliberately conservative. Explicitly correlated calculations have long described ground and excited two-electron states of helium, including radial and angular correlation effects . The cumulant of the 2-RDM is an established representation of information beyond the antisymmetrized product of one-particle densities . Time-dependent natural-orbital occupations, pair densities, TD-2RDM propagation, and time-dependent full configuration interaction have all been used to study correlated electronic dynamics .

These works motivate the present study but also delimit its novelty. The proposed gap is not a lack of methods for calculating dynamic correlation. Rather, it is the absence of a standard diagnostic specifically organized around the following sequence:

$$\Gamma(t) \rightarrow \Lambda(t) \rightarrow \|\Lambda(t) - \Lambda_R\|_F,$$

where R is a physically selected reference state and the resulting scalar is followed continuously through a radiative pathway.

To the best of the present survey, such a reference-state correlation-distance trajectory has not become a standard diagnostic for atomic radiative cascades. This statement is intentionally narrower than a claim of general novelty in dynamic correlation, RDM theory, or cumulant measures.

Two-electron Hamiltonian and CI representation

For a helium-like atom with nuclear charge Z, the nonrelativistic field-free Hamiltonian is

$$\hat{H}_0 = \hat{h}(1) + \hat{h}(2) + \hat{V}_{12},$$

where

$$\hat{h}(i) = -\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i},$$

and

$$\hat{V}_{12} = \frac{e^2}{4\pi\epsilon_0 r_{12}}.$$

During excitation, an external electric field can be represented in the dipole approximation by

$$\hat{H}(t) = \hat{H}_0 + eE(t)(z_1 + z_2),$$

up to the chosen sign convention for the electronic charge.

The time-dependent Schrödinger equation is

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



A CI expansion is

$$|\Psi(t)\rangle = \sum_{\alpha} C_{\alpha}(t) |\Phi_{\alpha}\rangle,$$

with

$$i\hbar\dot{C}_{\alpha}(t) = \sum_{\beta} H_{\alpha\beta}(t)C_{\beta}(t).$$

The CI matrix contains the electron–electron interaction through

$$H_{\alpha\beta}^{(ee)} = \langle \Phi_{\alpha} | \frac{e^2}{4\pi\epsilon_0 r_{12}} | \Phi_{\beta} \rangle.$$

In second quantization,

$$\hat{H} = \sum_{pq} h_{pq} a_p^{\dagger} a_q + \frac{1}{2} \sum_{pqrs} \langle pq || rs \rangle a_p^{\dagger} a_q^{\dagger} a_s a_r,$$

where the antisymmetrized two-electron integral is

$$\langle pq || rs \rangle = \frac{e^2}{4\pi\epsilon_0} (\langle pq | r_{12}^{-1} | rs \rangle - \langle pq | r_{12}^{-1} | sr \rangle).$$

Reduced density matrices and the correlation cumulant

For a normalized two-electron pure state, define the one-particle RDM by

$$\gamma(x; x'; t) = 2 \int dx_2 \Psi(x, x_2; t) \Psi^*(x', x_2; t),$$

so that $\text{Tr} \gamma = 2$. The two-particle RDM is written as

$$\Gamma(x_1, x_2; x_1', x_2'; t) = 2 \Psi(x_1, x_2; t) \Psi^*(x_1', x_2'; t),$$

with the corresponding normalization convention kept fixed throughout the calculation.

The spin-summed pair density is

$$P(r_1, r_2; t) = \sum_{\sigma_1 \sigma_2} |\Psi(r_1, \sigma_1; r_2, \sigma_2; t)|^2.$$

Schematically, the 2-RDM may be separated as

$$\Gamma = \Gamma_{\text{ref}} + \Lambda, \quad \text{label \{eq:cumulant\}}$$

where Γ_{ref} is the antisymmetrized product constructed from the 1-RDM and Λ is the two-particle cumulant. The exact prefactors depend on the RDM normalization convention; therefore all quantities in the numerical implementation must use one convention consistently.

The decomposition emphasizes the distinction

$$\text{Coulomb interaction} \neq \text{exchange} \neq \text{genuine correlation}.$$



The cumulant is an established measure of information in the 2-RDM that cannot be reconstructed from the corresponding one-particle quantity alone .

Reference-state correlation distance

Let Λ_R be the cumulant of a selected reference state R. We define

$$\Delta\Lambda(t) = \Lambda(t) - \Lambda_R$$

and the proposed correlation distance

$$C_R(t) = \|\Lambda(t) - \Lambda_R\|_F,$$

where

$$\|A\|_F = \sqrt{\text{Tr}(A^\dagger A)}.$$

For the present application the ground state is chosen as the reference, so $R = G$ and $C_G = 0$.

The quantity C_G should not be confused with the absolute magnitude of electron correlation. A state may be strongly correlated and nevertheless have a small C_G if its correlation structure resembles the ground-state structure. Conversely, a state may have a moderate absolute cumulant norm while being far from the ground-state cumulant.

For $C_R \neq 0$,

$$\dot{C}_R = \frac{\Re \text{Tr}[\Delta\Lambda^\dagger \dot{\Lambda}]}{C_R}.$$

Thus $\dot{C}_R < 0$ denotes motion toward the reference structure and $\dot{C}_R > 0$ motion away from it. At $C_R = 0$, the squared distance

$$C_R^2 = \text{Tr}(\Delta\Lambda^\dagger \Delta\Lambda)$$

can be used for numerical stability.

Why energy relaxation need not imply correlation relaxation

The instantaneous energy is

$$E(t) = \langle \Psi(t) | \hat{H} | \Psi(t) \rangle.$$

For radiative decay the mean atomic energy decreases, but there is no general requirement that the correlation distance decrease monotonically. In particular,

$$\dot{E} < 0 \quad \Rightarrow \quad \dot{C}_G < 0.$$

Energy is a scalar expectation value of the Hamiltonian, whereas C_G is a distance in a high-dimensional space of two-particle correlation structures. The two quantities therefore need not have identical trajectories.

This distinction is the physical basis of the proposed analysis: an atom may lose energy while temporarily moving farther from the reference correlation structure.

Analytical two-configuration model

Consider

$$|\Psi(t)\rangle = a(t)|A\rangle + b(t)|B\rangle, \quad |a|^2 + |b|^2 = 1,$$



with

$$H = (E_A \ V \ V^* \ E_B).$$

For real V , define

$$\Delta = E_A - E_B, \quad \Omega = \frac{1}{\hbar} \sqrt{\Delta^2 + 4V^2}.$$

For $a(0) = 1$ and $b(0) = 0$,

$$|b(t)|^2 = \frac{4V^2}{\Delta^2 + 4V^2} \sin^2\left(\frac{\Omega t}{2}\right).$$

Writing

$$a = \sqrt{p}, \quad b = e^{i\phi} \sqrt{1-p},$$

shows that the 2-RDM contains coherence terms proportional to $ab^* = \sqrt{p(1-p)}e^{-i\phi}$. Hence equal populations can correspond to different 2-RDMs when their relative phases differ.

Therefore,

configuration populations do not uniquely determine the two – electron correlation structure.

This provides the analytical motivation for following the RDM rather than populations alone.

Minimal CI representation of the helium states

A common one-electron basis should be used for all states. A transparent minimal demonstration basis is

$$B_0 = \{1s, 2s, 3s, 2p, 3p, 3d\}.$$

The purpose is methodological rather than spectroscopic: a production calculation must enlarge the basis systematically.

Prototype states and representative symmetry-allowed correlation configurations.

State	Dominant configuration	Representative additional CSFs
G	$1s^2\ ^1S_0$	$1s2s, 2s^2, 2p^2\ ^1S, 3d^2\ ^1S$
P	$1s2p\ ^1P_1^o$	$1s3p, 2s2p, 2s3p, 2p3d$
D	$1s3d\ ^1D_2$	$2s3d, 2p^2\ ^1D, 2p3p\ ^1D, 3d^2\ ^1D$

For each symmetry sector,

$$|\Psi_X\rangle = \sum_{\alpha \in X} C_\alpha^{(X)} |\Phi_\alpha^{(X)}\rangle,$$

and

$$H_X C_X = E_X C_X.$$

The RDMs follow directly from the CI coefficients:



$$\gamma_{pq}^{(X)} = \sum_{\alpha\beta} C_{\alpha}^{(X)*} C_{\beta}^{(X)} \langle \Phi_{\alpha} | a_q^{\dagger} a_p | \Phi_{\beta} \rangle,$$

and

$$\Gamma_{pq,rs}^{(X)} = \sum_{\alpha\beta} C_{\alpha}^{(X)*} C_{\beta}^{(X)} \langle \Phi_{\alpha} | a_s^{\dagger} a_r^{\dagger} a_q a_p | \Phi_{\beta} \rangle.$$

The cumulant is then constructed from the same convention for every state.

Prototype radiative cascade in helium

We choose

$$|G\rangle = 1s^2\ ^1S_0, \quad |P\rangle = 1s2p\ ^1P_1^{\circ}, \quad |D\rangle = 1s3d\ ^1D_2.$$

NIST tabulates the $1s2p\ ^1P_1^{\circ}$ level at $171134.8970\text{ cm}^{-1}$ and the $1s3d\ ^1D_2$ level at $186104.9668\text{ cm}^{-1}$; the persistent $1s3d\ ^1D_2 \rightarrow 1s2p\ ^1P_1^{\circ}$ line is listed at $6678.1517\text{ \AA}$ with $A = 0.6369 \times 10^8\text{ s}^{-1}$.

The prototype cascade is therefore

$$D \rightarrow P \rightarrow G.$$

It is important not to treat $D \rightarrow G$ as a competing ordinary electric-dipole transition: the selected cascade is used precisely because the intermediate P state provides the allowed radiative pathway.

At the population level, a simple sequential-decay model gives

$$\dot{P}_D = -\Gamma_D P_D, \quad \dot{P}_P = \Gamma_D P_D - \Gamma_P P_P, \quad \dot{P}_G = \Gamma_P P_P.$$

For $P_D(0) = 1$,

$$P_D(t) = e^{-\Gamma_D t},$$
$$P_P(t) = \frac{\Gamma_D}{\Gamma_P - \Gamma_D} (e^{-\Gamma_D t} - e^{-\Gamma_P t}),$$

and

$$P_G(t) = 1 - P_D(t) - P_P(t).$$

These equations describe populations only; they do not determine $\Lambda(t)$.

Correlation trajectory for the cascade

Let $\rho(t)$ denote the reduced density operator in the selected cascade-state space,

$$\rho(t) = \sum_{i,j=D,P,G} \rho_{ij}(t) |i\rangle\langle j|.$$

The corresponding 2-RDM is obtained as

$$\Gamma(t) = \sum_{ij} \rho_{ij}(t) \Gamma_{ij},$$

followed by



$$\gamma(t) = \text{Tr}_2 \Gamma(t)$$

and construction of $\Lambda(t)$.

The central scalar is then

$$C_G(t) = \|\Lambda(t) - \Lambda_G\|_F.$$

For convenient comparison between pathways,

$$R(t) = \frac{C_G(t)}{C_G(0)}$$

may be used when the initial state is D. Thus $R(0) = 1$, whereas $R = 0$ corresponds to the ground-state correlation structure in the selected common representation.

A full correlation-space path length is

$$L_\Lambda = \int \|\dot{\Lambda}(t)\|_F dt.$$

The scalar-distance path length is

$$L_C = \int |\dot{C}_G(t)| dt.$$

The first retains more information than the second; the latter is easier to visualize.

Excitation versus relaxation

If an external field prepares the excited state, the correlation structure may follow a path

$$\Lambda_G \rightarrow \Lambda_1 \rightarrow \Lambda_2 \rightarrow \Lambda_D.$$

Radiative relaxation may subsequently follow

$$\Lambda_D \rightarrow \Lambda'_2 \rightarrow \Lambda'_1 \rightarrow \Lambda_G.$$

There is no general requirement that $\Lambda_i = \Lambda'_i$. The difference can be quantified through

$$L_{\text{exc}} = \int \|\dot{\Lambda}_{\text{exc}}\|_F dt, \quad L_{\text{rel}} = \int \|\dot{\Lambda}_{\text{rel}}\|_F dt,$$

and the dimensionless path-asymmetry parameter

$$A_\Lambda = \frac{|L_{\text{exc}} - L_{\text{rel}}|}{L_{\text{exc}} + L_{\text{rel}}}.$$

This is a geometric diagnostic, not a thermodynamic irreversibility measure.

A useful visualization is the parametric curve

$$(E(t), C_G(t)).$$

It allows energetic and correlation-space relaxation to be examined simultaneously.

Natural occupations and pair density as complementary diagnostics

Natural orbitals satisfy

$$\gamma \varphi_i = n_i \varphi_i,$$

with



$$\sum_i n_i = 2.$$

Natural occupations are valuable because they reveal changes in the one-particle distribution, and time-dependent natural-orbital dynamics have already been studied in atomic strong-field problems . They do not, however, uniquely specify the full 2-RDM.

The pair density

$$P(r_1, r_2; t)$$

provides a complementary coordinate-space picture and has been used to separate exchange and Coulomb correlation in time-dependent helium calculations . The proposed $C_G(t)$ should therefore be compared with both natural occupations and pair-density observables in a future numerical implementation.

Convergence and numerical protocol

The minimal CI space is only a starting point. Let N denote the size of the orbital/CI space. A calculation should be enlarged according to

$$B_0 \subset B_1 \subset B_2 \subset \dots$$

Energy convergence requires

$$|E_X^{N+1} - E_X^N| < \epsilon_E,$$

while the actual correlation observable requires

$$\|\Lambda_X^{N+1} - \Lambda_X^N\|_F < \epsilon_\Lambda$$

and

$$|C_X^{N+1} - C_X^N| < \epsilon_C.$$

Energy convergence alone is therefore insufficient.

An independent-particle control can be generated by suppressing the explicit electron–electron interaction in the Hamiltonian. The resulting calculation should be compared carefully with the interacting case because antisymmetry and exchange remain properties of the fermionic state even when the Coulomb term is removed.

For quantitative calculations, time-dependent CI and TD-2RDM methods provide two natural computational routes . The choice between them should be based on the desired treatment of radiative decay, coherence, and the size of the configuration space.

Testable predictions and interpretation

The framework is deliberately formulated without assuming a particular numerical outcome. Several possibilities can be distinguished.

First, $C_G(t)$ may decrease approximately monotonically during the cascade. In that case energy relaxation and reference-state correlation relaxation are correlated for the selected pathway.

Second, the intermediate state may satisfy

$$C_P > C_D,$$

indicating that the cascade temporarily moves farther from the ground-state correlation structure.



Third, $C_G(t)$ may be nonmonotonic even while $E(t)$ decreases monotonically. This would provide a direct example of energetic relaxation accompanied by a correlation-space excursion.

Fourth, excitation and relaxation may give different path lengths, $L_{\text{exc}} \neq L_{\text{rel}}$. Such a result would indicate pathway asymmetry in the chosen correlation representation.

Finally, two times may have similar populations but different 2-RDMs. This would demonstrate explicitly that population dynamics are insufficient to characterize the complete correlated state.

None of these possibilities is asserted as a result of the present paper. They are the numerical tests that define the proposed research program.

Relation to entanglement and pairing

The proposed quantity should not automatically be called an entanglement measure. The 2-RDM cumulant contains information associated with correlation and can capture contributions related to spin entanglement, but the reference-distance C_G is a geometric comparison between two cumulants rather than a standard entanglement monotone.

Likewise, no Cooper-like pairing assumption is made. The correlated two-electron state of helium arises from antisymmetry, the Coulomb interaction, and the atomic Hamiltonian. The term “two-electron correlation” is therefore preferred to “pairing” throughout this work.

Limitations

Several limitations should be kept explicit. First, the numerical value of the cumulant and its Frobenius norm depends on the adopted RDM normalization convention. Second, direct subtraction of cumulants requires a common orthonormal one-particle basis. Third, a scalar distance compresses a high-dimensional matrix trajectory and therefore cannot uniquely characterize the complete correlation structure. Fourth, the three-state cascade is a reduced model; real helium dynamics can involve additional bound, metastable, and continuum states. Fifth, the present paper does not calculate spontaneous emission from first-principles QED. The radiative dynamics must be supplied by an appropriate open-system, master-equation, or QED treatment. Finally, no numerical correlation trajectory is claimed here.

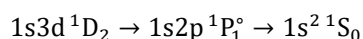
Conclusions

We have formulated a reduced-density-matrix framework for studying dynamical reorganization of two-electron correlation during atomic excitation and radiative relaxation. The central quantity is the reference-state correlation distance

$$C_R(t) = \|\Lambda(t) - \Lambda_R\|_F.$$

The quantity is constructed entirely from established RDM and cumulant concepts; the proposed element is its use as a trajectory diagnostic for atomic excitation and cascade relaxation.

An analytical two-configuration model demonstrates why orbital populations do not uniquely determine the complete two-electron density matrix. The helium sequence



provides a concrete experimentally anchored prototype. The framework separates energy relaxation from correlation-space relaxation and provides quantitative path measures for comparing excitation and decay.

The next decisive step is a converged CI or TD-2RDM calculation of Λ_G , Λ_P , Λ_D , and subsequently $\Lambda(t)$. The scientific outcome should be determined by that calculation rather than assumed in advance. In this form, the



proposed framework provides a compact and falsifiable route for testing whether atomic relaxation possesses characteristic organization in two-electron correlation space.

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