LETTER TO THE EDITOR

Measure of electron–electron correlation in atomic physics

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Abstract. We propose a criterion to determine the numerical degree of global (non-operator-specific) correlation of a multiparticle quantum system and apply it to several situations, including electron–atom scattering and strong-field photoionization. We show that the degree of correlation tends to increase in the presence of the field.

Questions of correlation in many-body systems are pervasive in physics. For example, how much information about a given system is conveyed by single-particle functions, or by two-point correlations, or how many N-particle canonical functions are required to construct the system's true N-body wavefunction? Is a given excitation spectrum describable by one-particle functions alone, or do higher order correlations or new quantum numbers play an essential role?‡

The existence of electron correlation is the source of everything deep and still mysterious in multi-electron atomic physics. Without an irreducible core of electron correlation every atomic process would be governed by effective one-particle physics. The creation of strongly correlated states in the laboratory is often a difficult experimental task, and the analysis of multiparticle experimental data in terms of specified correlation functions is in general an unsolved problem. But, in addition to these well recognized practical problems, there are purely theoretical questions that in our opinion have not been satisfactorily addressed regarding system-global (not operator-specific) correlation: (i) how to decide which of two N-body physical states is more correlated, and by precisely how much? (ii) what quantity serves as a suitable *degree of correlation*? (iii) does correlation change in time in an interesting way? and perhaps most important, (iv) can external parameters be used to manipulate or control correlation, perhaps leading to entirely new types of atomic physics experiments? Some discussion of these questions appears to be necessary, particularly in matters of correlation control. There must be two parts to any such discussion—how to calculate global multiparticle properties such as the wavefunction correctly, and how to calculate a degree of correlation from the wavefunction. We will begin with the second part.

There are various ways to speak of correlation in the context of stationary problems (for example, see [3]). Typically correlation is associated with the extent to which predictions of a specific approximate theory disagree with exact results. A common example is the

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‡ The description of doubly and triply excited electron states in atoms is a good example. The modern era of correlation in atomic physics began with the experiments of [1], which demonstrated convincingly that a helium atom with both electrons excited could not be satisfactorily characterized by hydrogenic quantum numbers, and the corresponding theoretical analysis of [2].

concept of correlation energy. This simply refers to the amount by which a single single-configuration Hartree–Fock calculation overestimates the exact energy. In this letter we propose a measure of correlation both more precise and more global than this, in the sense that it follows from the system wavefunction itself, and requires no comparison with any specific approximate theory or reference to any specific variable such as energy. One important consequence is that it can be generalized straightforwardly to time-dependent situations, including laser excitation, as we will show.

Naturally one cannot expect to pin a unique meaning to such a common word in physics as correlation, but our proposed definition of a *degree of correlation* has simple and attractive properties, and we will describe some applications of it. The proposed definition is applicable to all many-particle fermionic and bosonic systems. For simplicity we will discuss it here in the 'smallest' fundamental context, a two-electron atom. This is the context closest to correlation control via laser excitation, and also one with long-standing interest [4, 5].

Let the exact two-electron wavefunction be $\Psi(x_1, x_2)$. The so-called 'canonical representation' [6] of Ψ is characterized by a sum over only a single-particle index†

$$\Psi(x_1, x_2) = \sum_\alpha D_\alpha b_\alpha(x_1, x_2) \tag{1}$$

where $b_\alpha(x_1, x_2)$ is a Slater determinant of specific orthonormal single-particle orbitals for fermions and a product of identical orbitals for bosons. In strong contrast to usual basis set expansions, given $\Psi(x_1, x_2)$, the *canonical representation is unique*, and its uniqueness is the key to our proposal. We identify the amount of correlation roughly with the 'number' of different functions b_α necessary to construct the exact two-particle wavefunction. It is not difficult to build up from this rough idea several precise definitions (which will be time dependent because Ψ is time dependent, even though we do not indicate it). We have proceeded as follows. The normalization for $\Psi(x_1, x_2)$ leads to the obvious condition for the coefficients $\sum_\alpha |D_\alpha|^2 = 1$, which shows that each squared coefficient can be interpreted as a weight (probability). The *average* probability $|D_\alpha|^2$ is then given by $\sum_\alpha |D_\alpha|^4$. The inverse of this is the 'number' of effectively non-zero probabilities, so a *degree of correlation* K is defined in this way:

$$K \equiv \left[\sum_\alpha |D_\alpha|^4 \right]^{-1}. \tag{2}$$

In contrast to some other similar and also 'natural' definitions, K has the following desirable properties: (a) it is independent of the representation of the wavefunction, so that, for example, K is the same in configuration and momentum space; (b) K is also gauge invariant, which is important for systems in the presence of electromagnetic (laser) fields; and (c) it obviously achieves its minimum value of 1 for the least correlated state, a single Slater determinant‡.

Although K has attractive properties, there is still a question how to compute it, even if we know the exact two-electron wavefunction $\Psi(x_1, x_2)$, because Ψ will typically not be expressed in canonical form. The key role is played by the single-particle density operator

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† The superposition given in (1) is sometimes called the Schmidt decomposition [7].

‡ Note that the Slater determinant itself embodies antisymmetry, or 'Pauli correlation' which is not counted by K.

$\rho(x, x')$ which is obtained from the total density matrix $\Psi \otimes \Psi^*$ by integrating out all particle coordinates and spins with the exception of those for one particle:

$$\rho(x, x') \equiv \int dx_2 \, \Psi(x, x_2)\Psi^*(x', x_2). \tag{3}$$

The operator $\rho(x, x')$ is Hermitian and its eigenvalues are the desired coefficients $|D_\alpha|^2$. [For N fermions each eigenvalue is N-fold degenerate and has to be multiplied by N to give $|D_\alpha|^2$.]

The single-particle ρ provides both a constructive route to calculation of K and an alternative interpretation of K via statistical mechanics. Starting from the symmetric two-particle wavefunction $\Psi(x_1, x_2)$, if the reduced density matrix ρ corresponds to a pure single-particle state [tr $\rho^2 = 1$] then $K = 1$ and the state Ψ is uncorrelated. This means that tracing out the second electron's coordinates does not decrease the information about the first one in the full wavefunction. On the other hand a mixed state for ρ[tr $\rho^2 < 1$] gives $K > 1$ and indicates a correlated state Ψ. This is clear because the two-particle correlation 'mixes' otherwise independent particle orbitals and K reflects the information loss due to tracing. *In fact, the logarithm of K is sometimes called Stückelberg entropy.*

To illustrate the meaning of K purely qualitatively, consider a two-particle wavefunction whose relative-coordinate wavepacket is tightly localized but whose center-of-mass wavepacket is very broad. Obviously the system is in a highly correlated (large K) two-particle state. Even though we have little information about the location of either particle separately, if we find one of them we have practically found the other. Conversely, in other words, if we trace out the first particle's coordinates the other particle can only be located somewhere within the range of the (large) centre-of-mass packet. So the one-particle tracing induces a great loss of information, which is reflected in the large K of the original state.

More quantitative work requires two-particle wavefunctions. A context of particular interest recently is two-electron systems in strong laser fields. A key question is whether or when strong radiative forces can compete with e–e repulsion and influence correlation. Burnett [8] has taken a step in this direction by solving for the wavefunction of double ionization in a stripped-down two-electron model without invoking Hartree–Fock methods. His results provide a useful critique of standard time-dependent two-electron theory in laser fields. Kulander *et al* [9], have discussed carefully the inevitable flaws in Hartree–Fock methods in the context of ionization, in which case the continuous decrease in bound electron probability erroneously alters the strength of the core potential. Pindzola *et al* [9], have compared exact and time-dependent Hartree–Fock wavefunctions calculated for photoionization of a one-dimensional two-electron atom†

We now use basically the same model to evaluate K in a number of instances of interest. As a reminder [11, 12], the Hamiltonian whose wavefunctions we will use is

$$H = \tfrac{1}{2}p_1^2 + \tfrac{1}{2}p_2^2 - Z/(x_1^2 + 1)^{1/2} - Z/(x_2^2 + 1)^{1/2} + 1/[(x_1 - x_2)^2 + 1]^{1/2}. \tag{4}$$

It describes the interaction of two electrons with each other and each of them with a nucleus of positive charge Z via the same smoothed 1D Coulomb potential $1/(x^2 + 1)^{1/2}$. Since we start in the ground state, and there are no spin interactions, we can take the spatial part of the wavefunction $\Psi(x_1, x_2)$ to be symmetric.

First we have calculated K for the ground state for $Z = 1, 2$ and 3. With increasing nuclear charge Z one would expect that e–e correlations become less and less important

† Details of such 1D atoms have already been explored in the single-electron case. See, for example [11].
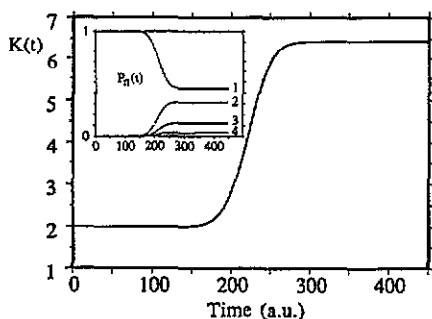
Figure 1. Growth of correlation during inelastic Franck–Hertz scattering. The inset shows the corresponding time dependence of excited H level probabilities $P_n(t)$.

as the electron–nucleus interaction becomes more dominant. This expectation is indeed confirmed by the numerical values for K. The model 'negative ion' ($Z = 1$) has a significant ground state correlation, $K = 1.10$, but the ground states for $Z = 2$ and 3 have much smaller values, $K = 1.01$ and 1.007, respectively. Indeed, when applied to these 'atoms', Hartree–Fock theory makes an error of 5.1% in the $Z = 1$ ground state energy, whereas it gives all other ground state energies ($Z = 2, 3, 4 \ldots$) almost perfectly [13].

We have also calculated the energy expectation in the most significant canonical basis state b_α (constructed from the leading eigenvector of the one-electron density matrix). The value was off by 5.4% from the exact result, and thus was slightly less accurate than the value computed from the corresponding Hartree–Fock state. This illustrates that $\rho(x, x')$ is not designed with energies in mind, whereas the Hartree–Fock states are constructed to minimize the energy uncertainty of the Hamiltonian.

We now extend the discussion to encompass time dependences. We must emphasize that, due to the uniqueness of the superposition in (1) for each Ψ, the basis states are different at each moment in time. Again there is a strong contrast with the more familiar situation in which a basis set is time-independent and the expansion coefficients carry all the information about changes in time. In our first example we have calculated K throughout the scattering experiment e + H($n = 1$) → e + H*, one of the most significant in atomic physics [14]†. Initially the two electrons are well separated and uncorrelated. We chose the incident kinetic energy too low to ionize the bound electron, in which case there must be two well separated electrons finally as well as initially. However, one expects the final state to be correlated. The interesting question is: what is the degree of final state Franck–Hertz correlation? Again, the soft-core 1D Coulomb interaction permits exact numerical solution of the time-dependent Schrödinger equation as an initial value problem, *and probably for the first time in non-trivial two-electron scattering*. Thus K can be calculated exactly from the distant past, throughout the interaction zone, and into the final state. The result is shown in figure 1. The dramatic rise in K by more than 4 occurs at the time of the e–H collision, and notably K does not decrease afterwards. This is as it should be. It is the multiplicity of orbitals available in the final state (even in 1D) that allows increased e–e correlation. The inset in figure 1 shows the populations of several states in H* through the course of the collision. In figure 2 we show the actual weights of the most significant eigenvalues of ρ at the end of the experiment.

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† Significant progress in the theory of e–H scattering has been achieved recently with large-basis close-coupling calculations by [15].
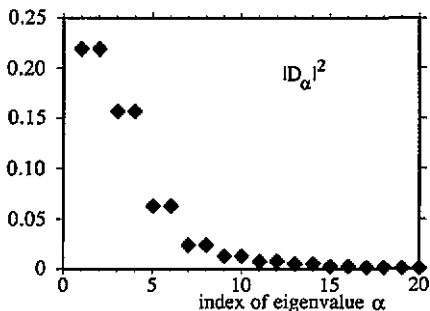
Figure 2. The eigenvalue distribution corresponding to the two-electron final state in the scattering experiment of figure 1.

Finally, we come to the question of laser control of correlation. We restrict our analysis here to the 'negative ion' ($Z = 1$) and calculate K for several numerical experiments that have already been reported elsewhere [12, 13]. In each case the two-electron system, initially in the ground state, is subjected to a laser pulse of duration 20 optical cycles and we have continued to monitor the time development of the wavefunction after the laser turn-off for 10 more optical cycles. We will discuss three different parameter regimes which differ by the degree of activity of the individual electrons.

The first regime [12] (low laser frequency) corresponds to one-photon detachment. The field is taken strong enough to detach the outer electron completely in 20 optical cycles, but weak enough to permit the deeply bound core electron to remain completely passive. Curve (a) in figure 3 shows growth to an asymptotic value close to $K = 2$, which indicates that it would be sufficient to describe this photodecay by single-electron theory using only two orbitals. Indeed, the largest two weights $|D_\alpha|^2$ contribute 99.7% to the norm.

The next regime is characterized by a detaching outer electron and an active but still bound core electron [12]. This situation can be achieved when the laser pulse is in resonance with a bound–bound transition of the core electron. Curve (b) of figure 3 grows well above $K = 2$. It is interesting to note that the core Rabi oscillations are manifest in the (periodic)
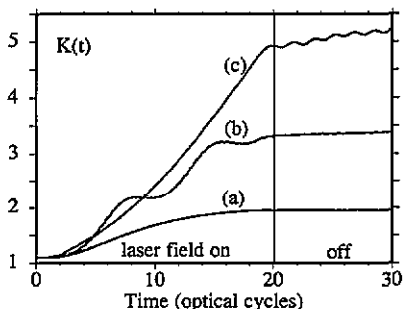

Figure 3. The correlation K as a function of time for three different regimes in laser intensity and frequency ω. The laser pulse has a two-cycle linear turn on and off and a constant field strength $\mathcal{E}$ between the second and eighteenth cycle. (a) The inner electron is passive and the outer electron is 98.4% photodetached under the absorption of a single photon ($\mathcal{E} = 0.005$ au, $\omega = 0.08$ au). (b) The inner electron is mainly bound but very active and the outer electron is 85.5% photodetached ($\mathcal{E} = 0.05$ au, $\omega = 0.395$ au). (c) Both electrons are active and ionize rapidly with a detachment probability 85.3% and a double-ionization probability of 31.3% ($\mathcal{E} = 0.5$ au, $\omega = 1.0$ au).

growth spurts of correlation. In the last example (high photon frequency and greater field strength [12]) we enter a regime in which both electrons become appreciably ionized. In this regime direct one-photon double ionization, core shake-up and other processes are all possible, and K reaches a still larger value. It may be more reasonable to say that correlation is actually under control when one demonstrates an example in which K is induced to decrease rather than increase, but the examples in figure 3 do demonstrate the behaviour of a specific numerical measure of correlation, and they do demonstrate that it is notably sensitive to the parameters of an applied radiation field.

In summary, we believe that K provides a natural measure of correlation in a many-electron quantum system and also one that is easy to calculate, given any many-particle wavefunction. It provides a precise numerical index to judge to what degree approximate calculations have included correlation. Again we emphasize that K is basis-independent. As an example, the K parameter has been calculated [16] for the $4snd\,^1D_2$ Rydberg series with principal quantum number $n = 5$ to 24 of the Ca atom, using an *ab initio* MQDT method. These studies have given some first indication that the mixing of doubly and singly excited states manifests itself in an abnormally high value of K. It also turns out that the K parameter we introduced in this letter can be applied to measure quantum signatures of classical chaos on the level of a single quantum state. Of course, the single K parameter contains only partial information about correlation. Various higher moments and weighted measures of the eigenvalue distribution of ρ could also be analysed. In the three cases mentioned above the eigenvalues themselves fall off nearly exponentially.

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