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The hydrogen atom as an entangled electron–proton system

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We illustrate the description of correlated subsystems by studying the simple two-body hydrogen atom. We study the entanglement of the electron and proton coordinates in the exact analytical solution. This entanglement, which we quantify in the framework of the density matrix formalism, describes correlations in the electron–proton motion. © 1998 American Association of Physics Teachers.

I. INTRODUCTION

Independent particle models often provide a good starting point to describe the physics of many-particle systems. In these models, the individual particles behave as independent particles that move in a potential field that accounts for the interaction with the other particles in an average sense. However, depending on the systems and the properties that are studied, the results of the independent particle calculations are not always sufficiently accurate. In that case it is necessary to correct for the fact that the motion of a single particle depends on the positions of the other particles, rather than on some average density. Consequently, in a system of interacting particles, the probability of finding two particles with given positions or momenta is not simply the product of the single-particle probabilities: We say that the particles are “correlated.”

In a more general context, the problem can be formulated as the description of interacting subsystems (the single particle in the many-particle system being the example of the subsystem). A convenient theoretical framework to deal with this problem in quantum mechanics is provided by the density matrix theory, which is almost as old as quantum mechanics itself.^{1,2} The ever-present interest in density matrix theory, in spite of its long history, is justified by the power of its description and the importance of its applications, which extends to the study of the very foundations of quantum theory.^{1–3} In this article, we briefly review some important aspects of density matrix theory and we illustrate its use for describing correlations of interacting subsystems by studying the simple, exactly solvable system of the hydrogen atom.

II. SUBSYSTEMS AND QUANTUM CORRELATIONS

In very broad terms, giving the state of a physical system means providing the necessary information to evaluate all its observables quantitatively. The states of a quantum mechanical system are frequently represented by vectors of unit norm in a Hilbert space \mathcal{H} , in general of infinite dimension (hence their usual designation as “state vectors”). If the system is in a state $|\Psi\rangle$, with $\langle\Psi|\Psi\rangle=1$, the outcome of measurements of an observable quantity A has an expectation value $\langle A \rangle$ equal to

$$\langle A \rangle = \langle \Psi | \hat{A} | \Psi \rangle, \quad (1)$$

where we use a caret, “ \hat{A} ,” to distinguish the operator representing the observable from the observable itself. If the vectors $|w_i\rangle$, $i=1,2,\dots$ are a basis of the Hilbert space \mathcal{H} , we can use the completeness relation, $1 = \sum_m |w_m\rangle\langle w_m|$, to write the expectation value as

$$\langle A \rangle = \sum_{m,n} \langle \Psi | w_m \rangle \langle w_m | A | w_n \rangle \langle w_n | \Psi \rangle. \quad (2)$$

In matrix notation, the mn -matrix element of the \hat{A} operator in the $|w\rangle$ basis is equal to $\hat{A}_{mn} = \langle w_m | \hat{A} | w_n \rangle$. The remaining ingredients of Eq. (2) can be collected as $\rho_{nm} = \langle w_n | \Psi \rangle \times \langle \Psi | w_m \rangle$, known as the density matrix,^{1,4,5} which is recognized as the matrix representing the so-called density operator, $\rho = |\Psi\rangle\langle\Psi|$, in the chosen basis. The expectation value of Eq. (2) can then be written as

$$\langle A \rangle = \sum_{m,n} \hat{A}_{mn} \rho_{nm}, \quad (3)$$

which is the trace of the product of the A and ρ matrices, $\langle A \rangle = \text{Tr}(\hat{A}\rho)$. In this expression, the state of the system is represented by the density matrix or, equivalently, by the density operator ρ . The form of this operator, together with the normalization property of the underlying state vector $|\Psi\rangle$, lead to some important properties, which are of course shared by the corresponding density matrices. Namely, the density operator is a non-negative (meaning that $\langle \phi | \rho | \phi \rangle \geq 0$ for any vector $|\phi\rangle$) self-adjoint operator ($\rho = \rho^\dagger$), of unit trace [$\text{Tr}(\rho) = 1$], and idempotent (meaning that $\rho = \rho^2$, which follows from $|\Psi\rangle\langle\Psi| \Psi\rangle\langle\Psi| = |\Psi\rangle\langle\Psi|$).

The use of state vectors $|\Psi\rangle$ to describe the state of a quantum system is, however, not general enough to cover many frequently occurring situations. As we shall discuss below, a suitable generalization is provided by the density matrix language, if only we relax the idempotency requirement.

Often, when probing a system, only part of the total system is subjected to a measurement. For example, in a typical scattering experiment only the scattered particle is detected. The target system is left behind in a final state that could be different from its initial state, but this state is not observed directly. It is then natural to divide the total system into the target system and the single-particle system of the scatterer. Also, in many experiments involving mesoscopic, or semi-macroscopic, quantum devices, it is very hard, if not impossible, to ensure efficient isolation from the environment, which then plays the role of a second subsystem coupled to the system of interest.⁶ Mathematically, such partitioning of the system into subsystems means factoring the Hilbert space \mathcal{H} into the tensor product of the corresponding subspaces, $\mathcal{H} = \mathcal{H}_u \otimes \mathcal{H}_v$. If the \mathcal{H}_u and \mathcal{H}_v spaces are spanned, respectively, by the bases $|u_i\rangle$, $i = 1, 2, \dots$ and $|v_j\rangle$, $j = 1, 2, \dots$, then \mathcal{H} is spanned by the product states $|u_i\rangle|v_j\rangle$. Accordingly, a state vector $|\Psi\rangle$ describing the state of the system can be expanded as

$$|\Psi\rangle = \sum_{i,j} d_{i,j} |u_i\rangle|v_j\rangle. \quad (4)$$

Suppose now that one wishes to describe the state of one of the subsystems alone, say subsystem u . The observable quantities of this subsystem are represented by operators which act nontrivially on the vectors of \mathcal{H}_u while acting on the vectors of \mathcal{H}_v simply as the unit operator. The expectation value of such operators can be obtained from the reduced density matrix for the u system, which is defined as the trace of the full density matrix ρ over the v subspace. When the entire system is in the state described by $|\Psi\rangle$, this reads

$$\begin{aligned} \rho_u &= \text{Tr}_v \left(\sum_{i,j} \sum_{k,l} |u_i\rangle|v_j\rangle d_{i,j} d_{k,l}^* \langle u_k | \langle v_l | \right) \\ &= \sum_{i,k} \sum_j |u_i\rangle d_{i,j} d_{k,j}^* \langle u_k|. \end{aligned} \quad (5)$$

We can understand the trace as a sum \sum_j over the probabilities for the v subsystem to be in any possible $|v_j\rangle$ state. For example, in the scattering experiment where only the state of the detected particle is determined, the final state of the target (v) system is not measured, and one has to sum over the probabilities of finding the target in all possible $|v_l\rangle$ states.

An important limiting situation is that in which the overall state vector $|\Psi\rangle$ is itself a product of a u vector and a v vector, $|\Psi\rangle = |u\rangle|v\rangle$. For these product states, the density matrix $\rho = |\Psi\rangle\langle\Psi|$ becomes

$$\rho = |u\rangle|v\rangle\langle v|\langle u| = \rho^u \rho^v, \quad (6)$$

and the reduced density ρ^u is simply given by $|u\rangle\langle u|$. This is just of the form of a density operator associated with the state vector $|u\rangle$, which can then also be used to describe the state of the subsystem. In general, the state vector $|\Psi\rangle$ cannot be factored in this fashion, however. In this case one says that the two subsystems are in an ‘‘entangled’’ state. The density matrix of an entangled state does not factor and appears as a series of u and v products: The subsystems are correlated. The number of terms gives some indication of the departure from the uncorrelated density matrix, but as the number of terms depends on the choice of basis in the u and v spaces, this is not a good measure of correlation or entanglement. A way out of this difficulty is, however, provided by a simple and remarkable result due to Schmidt⁷ (see also Refs. 2, 8, and 9) which essentially identifies a ‘‘natural’’ basis (in the sense of being determined by the structure of the entangled state itself) in which the description of the entanglement is achieved with maximum simplicity.

The Schmidt basis is a product basis, in the usual sense that it is written as the tensor product of two particular bases, one for the \mathcal{H}_u space and another for the \mathcal{H}_v space. In order to find these two bases one looks for the eigenvectors of the reduced density matrices. If the state is not entangled, $|\Psi\rangle = |u\rangle|v\rangle$, ρ^u and ρ^v each have one single eigenvector of nonzero eigenvalue, $|u\rangle$ for ρ^u and $|v\rangle$ for ρ^v , and the numerical value of the corresponding eigenvalues is equal to 1. One then completes the basis in each subspace by including enough additional orthonormal vectors which are moreover orthogonal to the single ‘‘relevant’’ vector with nonzero eigenvalue. Each one of these additional basis vectors is then an eigenvector of the corresponding reduced density with eigenvalue zero, and the large degree of arbitrariness in choosing them reflects the large degeneracy of the corresponding eigenvalue zero. If, on the other hand, the subsystems are correlated, then ρ^u and ρ^v have a spectrum of nonvanishing eigenvalues. Interestingly, as we prove below, the eigenvalues of the ρ^u and ρ^v operators are the same. To see that, we assume that the ρ^u matrix in the $|u_i\rangle$ basis is diagonalized by the unitary transformation U ($\sum_i U_{il} U_{ij}^* = \delta_{lj}$; $\sum_i U_{li} U_{ji}^* = \delta_{jl}$),

$$\sum_k \rho_{ik}^u U_{kl} = \lambda_l U_{il}. \quad (7)$$

The ρ^u -matrix elements are given by Eq. (5), $\rho_{ik}^u = \sum_j d_{ij} d_{kj}^*$, so that Eq. (7) can be written as

$$\sum_{k,j} d_{ij} d_{kj}^* U_{kl} = \lambda_l U_{il}. \quad (8)$$

Multiplying Eq. (8) by d_{il}^* , and summing over i , we obtain

$$\sum_{i,j} \sum_k d_{il}^* d_{ij} d_{kj}^* U_{kl} = \lambda_l \sum_i d_{il}^* U_{il}. \quad (9)$$

Defining $V_{j,l} = \sum_k d_{kj}^* U_{kl}$, we find with Eq. (9) that the vector of components $(V_{1l}, V_{2l}, \dots, V_{jl}, \dots)$ is an eigenvector of ρ^v with eigenvalue λ_l :

$$\sum_j \rho_{l'j}^v V_{jl} = \lambda_l V_{l'l'}, \quad (10)$$

where $\rho_{l'j}^v = \sum_i d_{il'}^* d_{ij}$. It follows that ρ^u and ρ^v have the same eigenvalues λ . If the nonvanishing eigenvalues are not degenerate, then all these vectors are automatically orthogonal. And if, moreover, the set of eigenvectors with nonvanishing eigenvalue is still not complete, one still may complete the bases with additional orthogonal vectors which are again eigenvectors of the respective reduced densities with eigenvalue zero. Expanding $|\Psi\rangle$ in the product basis constructed in this way, which thus includes the eigenvectors $|u_\lambda\rangle$ of ρ^u and $|v_\lambda\rangle$ of ρ^v , $|\Psi\rangle = \sum_\lambda c_\lambda |u_\lambda\rangle |v_\lambda\rangle$, the reduced density matrices take on the form

$$\rho^u = \sum_\lambda |c_\lambda|^2 |u_\lambda\rangle \langle u_\lambda|, \quad (11)$$

which is diagonal and shows that the λ eigenvalues are equal to $\lambda = |c_\lambda|^2$. This also shows that the eigenvectors with zero eigenvalue do not participate in the expansion. The eigenvalues λ are thus both the probabilities of finding subsystem u in the states $|u_\lambda\rangle$ and the probabilities of finding subsystem v in the states $|v_\lambda\rangle$. The set of numbers $|c_\lambda|^2$ can therefore be interpreted as a distribution of occupation probabilities. In fact, the unit trace condition on the complete density operator ρ ensures that $\sum_\lambda |c_\lambda|^2 = 1$. For uncorrelated subsystems, there is just one nonvanishing probability and this distribution has a vanishing ‘‘width’’ or standard deviation. It is then reasonable to use the standard deviation as a measure of the correlation.¹⁰ Note that when the two subsystems are correlated, i.e., there is more than just one nonvanishing occupation probability $|c_\lambda|^2$, the reduced density matrix Eq. (11) is no longer idempotent, although all the other properties listed above for ρ still hold. As a result of this, the state of an entangled subsystem cannot be described in terms of a state vector in the corresponding Hilbert space, and one is forced to use the density matrix language. In this case one says that the subsystem is in a ‘‘mixed’’ state. ‘‘Pure’’ states, associated with definite state vectors, are, on the other hand, always associated with idempotent density operators.

In summary, the foregoing discussion shows that a subsystem of a larger quantum system is, in general, in a mixed state, even if the state of the system as a whole is pure. Furthermore, the Schmidt analysis shows that in this case the state of the complementary subsystem has exactly the same degree of impurity, in the sense that both reduced density matrices have the same spectrum. This corresponds to the impurity of both subsystems being due to their mutual entanglement in the given overall pure state. To the extent that a given quantum system is not really isolated, but interacts with other systems (possibly a nondescript ‘‘environment’’), this analysis also shows that assuming the purity of its state is inadequately restrictive. In the following section we examine the spatially homogeneous, but possibly not pure, states of a single quantum particle, independently of any dynamical processes that may in fact give real existence to such states. An example of such a dynamical process will be given next.

III. SINGLE-PARTICLE SYSTEM

For the sake of illustration, we apply the density matrix description to a single, ‘‘elementary’’ particle system. In spite of the extreme simplicity of this type of system, the density matrix language enables us to consider states that are not accessible within the standard state vector (or wave function) description—mixed states—which are of interest for the discussion of correlated many-particle systems.

In the coordinate representation, which corresponds to the choice of the eigenfunctions $|\mathbf{r}\rangle$ of the coordinate operator as basis, the density matrix ρ of a pure single-particle system represented by the state vector $|\Psi\rangle$, takes on the form

$$\rho(\mathbf{r}, \mathbf{r}') = \langle \mathbf{r} | \Psi \rangle \langle \Psi | \mathbf{r}' \rangle = \Psi(\mathbf{r}) \Psi^*(\mathbf{r}'), \quad (12)$$

where $\langle \mathbf{r} | \Psi \rangle = \Psi(\mathbf{r})$ is the wave function. In the general case, the single-particle density matrix is an object $\rho(\mathbf{r}, \mathbf{r}')$ with the properties of hermiticity, $\rho(\mathbf{r}, \mathbf{r}') = \rho^*(\mathbf{r}', \mathbf{r})$, unit trace, $\int d^3r \rho(\mathbf{r}, \mathbf{r}) = 1$, and non-negativity, $\int d^3r \int d^3r' \times \phi^*(\mathbf{r}) \rho(\mathbf{r}, \mathbf{r}') \phi(\mathbf{r}') \geq 0$. Note that idempotency is not being required in order to allow for mixed states.

We shall be concerned with a particular class of states which we shall refer to as homogeneous states. By definition, these states are translationally invariant, meaning that translation by an arbitrary position vector \mathbf{R} leaves the density matrix, and hence the state itself, unaltered: $\rho(\mathbf{r} + \mathbf{R}, \mathbf{r}' + \mathbf{R}) = \rho(\mathbf{r}, \mathbf{r}')$. As a consequence, all the density matrix elements depend only on relative positions, specifically, $\rho(\mathbf{r}, \mathbf{r}') = \rho(\mathbf{r} - \mathbf{r}')$. In this case, the Fourier transform $\tilde{\rho}(\mathbf{k})$ of $\rho(\mathbf{r} - \mathbf{r}')$,

$$\rho(\mathbf{r} - \mathbf{r}') = \frac{1}{(2\pi)^3} \int d^3k \tilde{\rho}(\mathbf{k}) \exp(i\mathbf{k} \cdot [\mathbf{r} - \mathbf{r}']), \quad (13)$$

plays a dual role in the description of the homogeneous state: (1) it is proportional to the momentum distribution of the system, and (2) it gives the eigenvalues of the density matrix. We shall now prove both assertions.

Let us first evaluate the expectation value $\langle \mathbf{p} \rangle$ of the momentum. If the system is pure and described by the quantum state $|\Psi\rangle$, then

$$\begin{aligned} \langle \mathbf{p} \rangle &= \int d^3r \Psi^*(\mathbf{r}) [-i\hbar \nabla] \Psi(\mathbf{r}) \\ &= -i\hbar \int d^3r d^3r' \delta(\mathbf{r} - \mathbf{r}') \nabla_{\mathbf{r}} \rho(\mathbf{r}, \mathbf{r}'). \end{aligned} \quad (14)$$

The trace prescription for calculating $\langle \mathbf{p} \rangle$, obtained above, is also valid for mixed states and inserting Eq. (13), we obtain

$$\begin{aligned} \langle \mathbf{p} \rangle &= -i\hbar \int d^3r \int d^3r' \delta(\mathbf{r} - \mathbf{r}') \nabla_{\mathbf{r}} \rho(\mathbf{r}, \mathbf{r}') \\ &= \frac{1}{(2\pi)^3} \int d^3r \int d^3r' \int d^3k [\hbar \mathbf{k}] \tilde{\rho}(\mathbf{k}) \\ &\quad \times \exp(i\mathbf{k} \cdot [\mathbf{r} - \mathbf{r}']) \delta(\mathbf{r} - \mathbf{r}'), \\ &= \frac{\Omega}{(2\pi)^3} \int d^3k [\hbar \mathbf{k}] \tilde{\rho}(\mathbf{k}), \end{aligned} \quad (15)$$

where we have used a large quantization volume Ω to avoid problems related to states of infinite norm. This normalization scheme, commonly called box normalization, assumes

that the particle is confined to a large volume Ω , which is taken to be infinite at the end of the calculation, $\Omega \rightarrow \infty$. A plane wave state is then normalized as $\exp(i\mathbf{k}\cdot\mathbf{r})/\sqrt{\Omega}$. Substituting $\mathbf{p}=\hbar\mathbf{k}$ in the integration of Eq. (15), we find that

$$\langle \mathbf{p} \rangle = \int d^3p \mathbf{p} f(\mathbf{p}), \quad (16)$$

where $f(\mathbf{p}) = [\Omega/(2\pi\hbar)^3] \tilde{\rho}(\mathbf{p}/\hbar)$. Similarly, the expectation value of higher-order powers of momentum components are equal to the corresponding higher-order moments of the $f(\mathbf{p})$ function, e.g., $\langle (\hat{\mathbf{p}}\cdot\hat{\mathbf{x}})^2 \rangle = \int d^3p (\mathbf{p}\cdot\hat{\mathbf{x}})^2 f(\mathbf{p})$. Thus, $f(\mathbf{p})$ may be interpreted as a momentum distribution function.

To see that $\tilde{\rho}(\mathbf{k})$ gives the eigenvalues of the density matrix, we use Eq. (13) to evaluate

$$\begin{aligned} & \int d^3r' \rho(\mathbf{r}-\mathbf{r}') \frac{\exp(i\mathbf{k}\cdot\mathbf{r}')}{\sqrt{\Omega}} \\ &= \frac{1}{(2\pi)^3} \int d^3k' \tilde{\rho}(\mathbf{k}') \frac{\exp(i\mathbf{k}'\cdot\mathbf{r})}{\sqrt{\Omega}} \int d^3r' \\ & \times \exp(i[\mathbf{k}-\mathbf{k}']\cdot\mathbf{r}') = \tilde{\rho}(\mathbf{k}) \frac{\exp(i\mathbf{k}\cdot\mathbf{r})}{\sqrt{\Omega}}, \end{aligned} \quad (17)$$

which we recognize as the eigenvalue equation of the density matrix [Eq. (7)] in coordinate representation. From Eq. (17), it follows that the eigenvectors of the density matrix are the plane wave states of momentum \mathbf{k} and that the corresponding eigenvalues are equal to $\tilde{\rho}(\mathbf{k})$.

The density matrix of a homogeneous single-particle system does *not* generally describe a pure system. To see that, we remind the reader that a pure system is characterized by an idempotent density matrix, $\rho^2 = \rho$. For the homogeneous single-particle system, this implies that the eigenvalues of the density matrix satisfy $\tilde{\rho}(\mathbf{k})^2 = \tilde{\rho}(\mathbf{k})$. Consequently, for a pure homogeneous single-particle system, we find that $\tilde{\rho}(\mathbf{k}) = 0$ or $\tilde{\rho}(\mathbf{k}) = 1$. Furthermore, the unit trace condition on the density matrix implies

$$\begin{aligned} 1 &= \int d^3r \rho(0) \\ &= \rho(0)\Omega = \frac{\Omega}{(2\pi)^3} \int d^3k \tilde{\rho}(\mathbf{k}) \rightarrow \sum_{\mathbf{k}} \tilde{\rho}(\mathbf{k}), \end{aligned} \quad (18)$$

where in the last step we reconverted the momentum integral to the sum of discrete momenta appropriate to the adopted volume quantization. Thus, the homogeneous single-particle system that is pure can only be described by a density matrix with a single eigenvalue, say $\tilde{\rho}(\mathbf{k}_1)$, equal to 1, and all other eigenvalues $\tilde{\rho}(\mathbf{k}) = 0$, $\mathbf{k} \neq \mathbf{k}_1$. Such a density matrix represents a particle with a definite momentum (zero standard deviation of the distribution of density matrix eigenvalues), corresponding to a plane wave wave function, $\langle \mathbf{r} | \Psi \rangle = \exp(i\mathbf{k}_1\cdot\mathbf{r})/\sqrt{\Omega}$. In contrast, an impure single-particle system has a spectrum $\tilde{\rho}(\mathbf{k})$ of density matrix eigenvalues. The standard deviation of the $\tilde{\rho}(\mathbf{k})$ distribution is a measure of the correlation or entanglement of the single-particle system.¹¹

It should be remarked, finally, that all the above discussion had a purely kinematical character, in the sense that we dealt with possible states of a quantum mechanical system and

with their inherent observable properties, without regard to any dynamical processes that might have led to their preparation. In the following section we consider a simple but definite composite dynamical system and use the tools developed here in order to study the entanglement effects generated by definite interaction processes.

IV. HYDROGEN ATOM

We now apply the density matrix formalism to stationary states of a system that can display correlation: the two-body hydrogen atom. The hydrogen atom consists of an electron and a proton, interacting by means of the Coulomb potential. The Hamiltonian of the electron-proton system is

$$\hat{H} = \frac{\hat{\mathbf{p}}_e^2}{2m_e} + \frac{\hat{\mathbf{p}}_p^2}{2m_p} - \frac{e^2}{|\mathbf{r}_e - \mathbf{r}_p|}, \quad (19)$$

where $\hat{\mathbf{p}}$ and \mathbf{r} denote the momentum and position operators in coordinate space, and the subscripts e and p indicate the electron and the proton.

In fact, the hydrogen atom can be treated as two uncorrelated subsystems. Transforming to relative, $\mathbf{r} = \mathbf{r}_p - \mathbf{r}_e$, and center-of-mass coordinates, $\mathbf{R} = (m_e\mathbf{r}_e + m_p\mathbf{r}_p)/M$, where M is the total mass, $M = m_e + m_p$, the Hamiltonian separates into a center-of-mass term which takes on the form of a free-particle Hamiltonian, $\hat{H}_{\text{cm}} = \hat{\mathbf{p}}_{\text{R}}^2/2M$, and an ‘‘internal’’ Hamiltonian which governs the relative motion of the electron and the proton, $\hat{H}_{\text{int}} = \hat{\mathbf{p}}_r^2/2m_r - e^2/r$, where m_r is the reduced mass, $m_r^{-1} = m_e^{-1} + m_p^{-1}$. The product of \hat{H}_{cm} and \hat{H}_{int} eigenstates,

$$\Psi(\mathbf{R}, \mathbf{r}) = \phi_{\text{int}}(\mathbf{r}) \exp\left(i \frac{\mathbf{P}}{\hbar} \cdot \mathbf{R}\right) / \sqrt{\Omega}, \quad (20)$$

is an eigenstate. According to the definitions introduced in Sec. II, the internal and center-of-mass subsystems for the state (20) are not correlated. If the hydrogen atom is in its atomic ground state, the internal wave function, ϕ_{int} , is equal to

$$\begin{aligned} \phi_{\text{int}}(\mathbf{r}) &= \frac{1}{\sqrt{\pi}} \left(\frac{1}{a_0}\right)^{3/2} \exp(-r/a_0) \\ & \text{(hydrogen in } 1s \text{ state)}, \end{aligned} \quad (21)$$

where a_0 is the Bohr radius, $a_0 = \hbar^2/m_r e^2$.

Partitioning the hydrogen atom differently into electron and proton subsystems gives an entangled state:

$$\Psi(\mathbf{r}_e, \mathbf{r}_p) = \phi_{\text{int}}(\mathbf{r}_e - \mathbf{r}_p) \exp\left(i \frac{\mathbf{P}}{\hbar} \cdot \frac{[m_e\mathbf{r}_e + m_p\mathbf{r}_p]}{M}\right) / \sqrt{\Omega}. \quad (22)$$

The reduced density matrix for the electron system can be obtained by taking the trace over the proton basis set of coordinate eigenfunctions:

$$\begin{aligned} \rho(\mathbf{r}_e, \mathbf{r}'_e) &= \int d^3r_p \Psi(\mathbf{r}_e, \mathbf{r}_p) \Psi^*(\mathbf{r}'_e, \mathbf{r}_p) \\ &= \exp\left(i \frac{m_e\mathbf{P}}{\hbar M} \cdot [\mathbf{r}_e - \mathbf{r}'_e]\right) \int d^3r_p \phi_{\text{int}}(\mathbf{r}_e - \mathbf{r}_p) \\ & \times \phi_{\text{int}}^*(\mathbf{r}'_e - \mathbf{r}_p) / \Omega \end{aligned}$$

$$= \exp\left(i \frac{m_e \mathbf{P}}{\hbar M} \cdot [\mathbf{r}_e - \mathbf{r}'_e]\right) \rho_{\text{int}}(\mathbf{r}_e, \mathbf{r}'_e), \quad (23)$$

where we introduce the electron density matrix ρ_{int} for electrons in atoms at rest ($\mathbf{P}=0$). It is interesting to note that the electron subsystem of the hydrogen atom is homogeneous. To prove that, it is sufficient to show that ρ_{int} depends on \mathbf{r}_e and \mathbf{r}'_e as $\mathbf{r}_e - \mathbf{r}'_e$. Substituting $\mathbf{r}'_e - \mathbf{r}_p = \mathbf{y}$ and writing the argument of ϕ_{int} , $\mathbf{r}_e - \mathbf{r}_p$, as $\mathbf{r}_e - \mathbf{r}'_e + \mathbf{y}$, we do indeed find that

$$\begin{aligned} & \int d^3 r_p \phi_{\text{int}}(\mathbf{r} - \mathbf{r}_p) \phi_{\text{int}}^*(\mathbf{r}'_e - \mathbf{r}_p) \\ &= \int d^3 y \phi_{\text{int}}(\mathbf{r}_e - \mathbf{r}'_e + \mathbf{y}) \phi_{\text{int}}^*(\mathbf{y}), \end{aligned} \quad (24)$$

which depends solely on $\mathbf{r}_e - \mathbf{r}'_e$. Consequently, the reduced electron density matrix (23) only depends on the relative position, indicating a homogeneous subsystem. This might appear surprising: We do not usually think of the electron in hydrogen as a homogeneous system. However, the reduced density matrix describes the observation of hydrogenic electrons in the assumption that the proton is “invisible.” Furthermore Eq. (22) describes a hydrogen of fixed momentum (e.g., a beam of hydrogen atoms of well-defined velocity) so that the center-of-mass position of the atom is undetermined. It is then equally likely to observe the electron in any position, and the electron subsystem is homogeneous.

Consequently, as discussed in the previous section, the Fourier transform of the density matrix plays a central role. The density-matrix ρ_{int} of a $1s$ electron in a hydrogen atom at rest [$\mathbf{P}=0$ in Eq. (23)], has a simple analytical Fourier transform,

$$\tilde{\rho}_{\text{int}}(\mathbf{k}) = \frac{1}{\Omega} \frac{64\pi a_0^3}{1 + (a_0 k)^2}. \quad (25)$$

The Fourier transform $\tilde{\rho}$ for an electron in an atom of arbitrary momentum \mathbf{P} is a translation in \mathbf{k} space of $\tilde{\rho}_{\text{int}}$. To show that, we insert the inverse Fourier transform of $\tilde{\rho}$ in the expression for the density matrix (23),

$$\begin{aligned} \rho(\mathbf{r}_e, \mathbf{r}'_e) &= \frac{1}{(2\pi)^3} \int d^3 k' \tilde{\rho}_{\text{int}}(\mathbf{k}') \\ &\times \exp\left(i \left[\frac{m_e \mathbf{P}}{M\hbar} + \mathbf{k}' \right] \cdot [\mathbf{r}_e - \mathbf{r}'_e]\right). \end{aligned} \quad (26)$$

The substitution, $\mathbf{k} = \mathbf{k}' + m_e \mathbf{P}/M\hbar$, then leads to the Fourier transform:

$$\begin{aligned} \rho(\mathbf{r}_e, \mathbf{r}'_e) &= \frac{1}{(2\pi)^3} \int d^3 k \tilde{\rho}_{\text{int}}\left(\mathbf{k} - \frac{m_e \mathbf{P}}{M\hbar}\right) \\ &\times \exp(i\mathbf{k} \cdot [\mathbf{r}_e - \mathbf{r}'_e]), \end{aligned} \quad (27)$$

from which it follows that

$$\tilde{\rho}(\mathbf{k}) = \tilde{\rho}_{\text{int}}\left(\mathbf{k} - \frac{m_e \mathbf{P}}{M\hbar}\right). \quad (28)$$

Thus, compared to $\tilde{\rho}_{\text{int}}$, $\tilde{\rho}$ is displaced in \mathbf{k} space by $m_e \mathbf{P}/M\hbar$. Similarly, the momentum distribution $f(\mathbf{p}) = [\Omega/(2\pi\hbar)^3] \tilde{\rho}_{\text{int}}(\mathbf{p}/\hbar)$, is related to the electron momen-

tum distribution $f_{\text{int}}(\mathbf{p})$ for atoms at rest, by means of a simple displacement in momentum space:

$$f(\mathbf{p}) = f_{\text{int}}\left(\mathbf{p} - \frac{m_e}{M} \mathbf{P}\right), \quad (29)$$

where

$$f_{\text{int}}(\mathbf{p}) = \frac{1}{(2\pi\hbar)^3} \frac{64\pi a_0^3}{1 + \left(\frac{a_0 p}{\hbar}\right)^2}. \quad (30)$$

Equation (29) expresses a Galilean transformation from the center-of-mass reference frame ($\mathbf{P}=0$) to the lab frame of reference in which the atom is moving with velocity \mathbf{P}/M . If the electron in the center-of-mass frame has velocity $\mathbf{v} = \mathbf{p}/m_e$, then, in the lab frame, its velocity is observed as $\mathbf{v}' = \mathbf{p}/m_e - \mathbf{P}/M$, corresponding to a momentum equal to $m_e \mathbf{v}' = \mathbf{p} - (m_e/M)\mathbf{P}$.

Since f and f_{int} are equal up to a translation in momentum space, their widths, or standard deviations, are equal. In the center-of-mass frame, $\langle \mathbf{p} \rangle = 0$, so that the standard deviation $\Delta p = \sqrt{\langle \mathbf{p}^2 \rangle - \langle \langle \mathbf{p} \rangle \rangle^2}$ is equal to

$$\Delta p = \sqrt{\int d^3 p p^2 f_{\text{int}}(\mathbf{p})} = \frac{\hbar}{a_0}. \quad (31)$$

Thus, although the electron subsystem is homogeneous, as a consequence of the electron–proton correlation, a measurement of the electron momentum can yield a finite range of values. In accordance with the Heisenberg uncertainty principle (the correlations confine the electron in the center-of-mass frame to a region of size $\sim a_0$) the size of this region in momentum space, or more precisely, the standard deviation Δp of the momentum distribution, equals \hbar/a_0 . In the context of describing correlating systems, Δp is a measure of the strength of the correlation: The stronger the electron and proton are correlated, the higher the value of a_0 and the larger the region in momentum space (Δp) over which the electron momentum is “spread out.”

V. CONCLUSION

In this paper, we have reviewed aspects of density matrix theory which pertain to the description of the entanglement of correlated subsystems. The mutual entanglement of subsystems of a larger (pure) system is conveniently quantified by the standard deviation of the reduced density matrix eigenvalues of the entangled subsystems. For the simple (but relevant) case of homogeneous single-particle subsystems, the density matrix eigenvalues give the particle’s momentum distribution. Thus the standard deviation of the momentum distribution is a measure of the entanglement of the single-particle system, as we have illustrated for the specific example of the electron in the two-body hydrogen atom.

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¹J. von Neumann, *Mathematical Foundations of Quantum Mechanics* (Princeton U.P., Princeton, 1955).

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- ¹⁰The degree of impurity of a state described by a density operator ρ is usually measured in terms of an entropy function, $S = -\text{Tr}(\rho \log \rho) = -\sum_{\lambda} (\lambda \log \lambda)$, $\{\lambda\}$ being the eigenvalues of ρ [see, e.g., V. Bužek, H. Moya Cessa, P. L. Knight, and S. J. D. Phoenix, "Schrödinger-Cat States in the Resonant Jaynes–Cummings Model: Collapse and Revival of Oscillations of the Photon-Number Distribution," Phys. Rev. A **45**, 8190–8203 (1992)]. This follows a procedure apparently first used by von Neumann (see Ref. 1), which was almost simultaneously adopted by S. Watanabe, "Application of the Thermodynamical Notions to Normal State of the Nucleus," Z. Phys. **113**, 482–513 (1939) to study the entanglement of individual nucleons in the actual stationary states of an atomic nucleus. This type of use of an entropy function was later spread by the work of Shannon [C. E. Shannon and W. Weaver, *The Mathematical Theory of Communication* (The University of Illinois Press, Champaign, IL, 1949)]. In more recent times use has also been made of the so-called "linear entropy" $\sigma = \text{Tr}(\rho - \rho^2) = 1 - \sum_{\lambda} \lambda^2$. This can be found, e.g., in P. C. Lichtner and J. J. Griffin, "Evolution of a Quantum System Lifetime of a Determinant," Phys. Rev. Lett. **37**, 1521–1524 (1976); W. H. Zurek, S. Habib, and J. P. Paz, "Coherent States via Decoherence," *ibid.* **70**, 1187–1190 (1993); J. I. Kim, M. C. Nemes, A. F. R. de Toledo Piza, and H. E. Borges, "Perturbative Expansions for Coherence Loss," *ibid.* **77**, 207–210 (1996). The standard deviation of the eigenvalues of ρ can be written as $\sum_{\lambda} \lambda^2 - 1/N^2$, where N is the number of nonvanishing eigenvalues λ , and is thus clearly related to the linear entropy. The essential ingredient in all these measures is a nonlinear dependence on ρ that makes it sensitive to the lack of idempotency of the density operator.
- ¹¹In the remainder of the paper, we choose to determine the standard deviation of the density matrix eigenvalues $\tilde{\rho}(\mathbf{k})$ in a manner that is different from the standard deviation, $\sum_{\lambda} \lambda^2 - 1/N^2$, in Ref. 10. In view of the close relationship between $\tilde{\rho}(\mathbf{k})$ and the momentum distribution $f(\mathbf{p})$, we choose to calculate the standard deviation of $f(\mathbf{p})$ as the width of the momentum distribution in \mathbf{p} space.