Molecular descriptors and quasi-distribution functions

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A R T I C L E   I N F O

A B S T R A C T

The concept of molecular quantum similarity is a rather subjective notion which depends on the definition of a molecular descriptor. Despite the vast set of options, today the main descriptor in use is the electron density usually provided by the time-independent Schrödinger equation. In this paper, an alternative definition of quantum similarity in the context of the Wigner formulation of quantum mechanics is suggested, based on a molecular descriptor defined in terms of quasi-distribution functions. We show that this definition has several important advantages over density based similarities. In particular, it offers a higher detailed description of a quantum system, thus refining the concept of similarity. To support our claim, we first present a theoretical example where two systems which appear to be similar, when using the density as a descriptor, become non-similar when their quasi-distributions are involved in the computation of the similarity. Moreover we simulate two quantum systems (utilizing the Wigner Monte Carlo method based on signed particles), i.e. a free Gaussian wave-packet and an H_2 molecule, and show that Wigner quasi-distribution functions provide a different perspective on the concept of quantum similarity.

1. Introduction

The notion of molecular quantum similarity was proposed in 1980 and, since then, a growing interest has been shown towards this concept [1]. As a matter of fact, nowadays it is utilized for practical purposes in many different fields such as organic, quantum and physical chemistry. It is interesting to note that different definitions of a quantum similarity can be provided depending on the context. For example, organic chemists may define two similar molecules when they have similar reactivity in certain reactions, while quantum chemists may focus on the molecular features, etc. Therefore, it is not surprising that it is difficult, if not impossible, to provide a universal definition of quantum similarity. In spite of that, it is important to have a practical definition even though it may be related to a particular context. For instance, in a pharmaceutical context molecular quantum similarity may provide a systematic way to investigate the relation between the structure of a molecule and its chemical reactivity, thus drastically easing the process of drug design and minimizing the occurrence of side effects.

While the concept of quantum similarity is becoming widespread in many communities and different definitions are being provided, to the best of our knowledge it seems that all directions taken so far are based on the Schrödinger (or standard) formulation of quantum mechanics [2]. However, different formulations exist which may offer a different perspective on the concept of quantum similarity [3–7]. In practice, in order to concretely (mathematically) define the concept of molecular quantum similarity, one has to define a *molecular descriptor* first. While an infinite set of options is available, for many practical and theoretical reasons, the electron density has become the most common choice [1].

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In this paper, we focus on the Wigner formulation of quantum mechanics which is equivalent to the Schrödinger approach but describes systems in terms of quasi-distribution functions instead of wave-functions. In particular, this approach provides a new molecular descriptor, the quasi-distribution function, which offers a very detailed time-dependent description of the system and, as such, allows the definition of a time-dependent quantum similarity. Moreover, recently a signed particle Monte Carlo method has been presented which is able to simulate the single-body time-dependent Wigner equation [8]. This method has been extended to be utilized in the context of density functional theory (DFT) [9] and even generalized to the many-body Wigner equation for ab-initio time-dependent simulations [10]. Therefore, it becomes possible to apply the concept of quantum similarity based on quasi-distribution functions in practical applications.

This paper is structured as follows. We first briefly sketch the Wigner formulation of quantum mechanics and its signed particle Monte Carlo method. We then proceed with some theoretical and numerical examples which clearly show the applicability of the quasi-distribution function as a molecular descriptor. In particular, we present one theoretical and two numerical examples where a quantum similarity based on the electron density would only provide a partial answer. Finally, we conclude with some comments on the suggested definition of molecular quantum similarity and its future development.

2. The Wigner Monte Carlo method

In this section, we briefly introduce the Wigner Monte Carlo (MC) method based on signed particles. For the sake of clarity, we restrict the exposition to a single particle in a one-dimensional configuration space. More mathematical details can be found in [8,10] for the single- and many-body Wigner equations respectively. For practical details on the implementation, the reader is invited to download the source code [11].

The purpose of the Wigner MC method is the resolution of the time-dependent single-body Wigner equation [8]. This equation describes the evolution of a quasi-distribution function $f_W = f_W(x; p; t)$ [3] and reads:

$$\frac{\partial f_W}{\partial t}(x; p; t) + \frac{p}{m} \cdot \frac{\partial f_W}{\partial x} = \int dp' f_W(x; p + p'; t) V_W(x; p'; t), \tag{1}$$

with $V_W = V_W(x; p; t)$ (the Wigner kernel) defined as:

$$V_W(x; p; t) = \frac{i}{\pi \hbar^2} \int d\xi e^{-\frac{2ip\xi}{\hbar}} [V(x + \xi; t) - V(x - \xi; t)], \tag{2}$$

and $V = V(x; t)$ the (time-dependent) potential acting upon the system.

By discretizing the momentum space p in multiples of the quantity $\Delta p = \frac{\hbar \pi}{L_C}$, with L_C specifying the momentum mesh, one can rewrite the semi-discrete Wigner equation as a Fredholm integral equation of second kind [8,10]:

$$f_W(x; M; t) - e^{-\int_0^t \gamma(x(y))dy} f_i(x(0); M) = \int_0^\infty dt' \sum_{M'=-\infty}^{+\infty} \int dx' f_W(x'; M'; t') \Gamma(x'; M; M')$$

$$\times e^{-\int_{t'}^t \gamma(x(y))dy} \theta(t - t') \delta(x' - x(t')) \theta_D(x'), \tag{3}$$

where the short notation $f_W(x; M; t)$ denotes the quantity $f_W(x; M\Delta p; t)$ and the quantity $\gamma = \gamma(x)$ reads:

$$\gamma(x) = \sum_{M=-\infty}^{\infty} V_W^+(x; M; t), \tag{4}$$

with V_W^+ the positive part of V_W and $f_i(x; M)$ the initial conditions of the system.

It is well-known that the solution of a Fredholm integral equation of second kind can be expressed as an infinite Liouville–Neumann series. As a consequence, the average value $\langle A \rangle$ of a macroscopic variable $A = A(x; p)$ can be written as a series as well. In particular, by writing down the first three terms of the series, it becomes clear that the expansion of $\langle A \rangle$ branches, and the total value is given by the sum of all branches:

$$\sum_{s=0}^{2} \langle A \rangle_s(\tau) = \int_0^\tau dt_i \int dx_i \sum_{M_i=-\infty}^{\infty} f_i(x_i; M_i) \underset{\Uparrow x_i, M_i, 0}{e^{-\int_0^{t_i} \gamma(x_i(y))dy}}$$

$$\times \left[A(x_1, M_i) \delta(t_i - \tau) + \int_{t_i}^\tau dt_1 \sum_{M_1=-\infty}^{\infty} \theta_D(x_1) \Gamma(x_1, M_1, M_i) \underset{\Uparrow x_1, M_1, t_i}{e^{-\int_{t_i}^{t_1} \gamma(x_1(y))dy}} \right.$$
$$\underset{\Uparrow x_1=x_i(t_i)}{}$$

$$\times \left. \left[A(x_2, M_1) \delta(t_1 - \tau) + \int_{t_1}^\tau dt_2 \sum_{M_2=-\infty}^{\infty} \theta_D(x_2) \Gamma(x_2, M_2, M_1) \underset{\Uparrow x_2, M_2, t_1}{e^{-\int_{t_1}^{t_2} \gamma(x_2(y))dy}} A(x_3, M_2) \delta(t_2 - \tau) \right] \right], \tag{5}$$
$$\underset{\Uparrow x_2=x_1(t_1)}{} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \underset{\Uparrow x_3=x_2(t_2)}{}$$

where the coordinates of a new trajectory are denoted by the symbol $\Uparrow$.