

Fractional Paradigms in Quantum Chemistry

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The realization of fractional quantum chemistry is presented. Adopting the integro-differential operators of the calculus of arbitrary-order, we develop a general framework for the description of quantum nonlocal effects in the complex electronic environments. After a brief overview of the historical and fundamental aspects of the calculus of arbitrary-order, various classes of fractional Schrödinger equations are discussed and pertinent controversies and open problems around their applications to model systems are detailed. We provide a unified approach toward fractional generalization of the quantum chemical models such as Hartree-Fock and Kohn-Sham density functional theory and develop fractional variants of the fundamental molecular integrals and correlation energy. Furthermore, we offer various strategies for modeling static- and dynamic-order quantum nonlocal effects through constant- and variable-order fractional operators, respectively. Possible directions for future developments of fractional quantum chemistry are also outlined.

I. Introduction

One of the central challenges in quantum chemistry is to find an efficient and accurate delineation of the electron correlation effects in many-body systems.^{1,2} Modern quantum chemical methods such as coupled-cluster have been successfully applied for the description of the electronic structure of systems with weak electron correlation. However, modeling strongly correlated electrons requires more sophisticated methodologies often suffering from the computational cost barrier problem in dealing with large systems.¹ Density matrix-based models, on the other hand, offer a compact representation of the electronic structure of many-body systems making them suitable candidates for large-scale computations. Nevertheless, the density-based models often have to deal with the N -representability problem.³

The study of chaotic and complex electronic environments in molecular systems becomes a more challenging subject when the electron correlation is dominated by the nonlocal effects of the surrounding complex molecular media with fractional dimensions.⁴ Memory effect⁵⁻⁷ and long-range correlation are two manifestations of such nonlocalities with respect to temporal and spatial fractional dimensions, respectively. An efficient way to account for these nonlocal effects is to go beyond classical calculus by replacing the integer-order differential and integral operators with their counterparts from the calculus of arbitrary-order.

During the past few decades, the calculus of arbitrary-order has witnessed a growing number of applications in different branches of physics⁷⁻⁹ such as optics,^{10,11} solid-state physics,^{12,13} and fluid dynamics.¹⁴ In particular, the possibility of adopting fractional operators in density functional theory (DFT) was raised by Dong,¹⁵ who developed a fractional variant of the Thomas-Fermi model and conjectured the validity of the Hohenberg-Kohn theorem within the framework of time-independent fractional quantum mechanics. Recently, numerical solutions to the Riemann-Liouville (RL) space-fractional Schrödinger equation (FSE) with Lennard-Jones¹⁶, Morse¹⁷, and Coulomb potentials¹⁸ have been computed for several model systems. In another investigation,¹⁹ the non-adiabatic effects in the fractional nuclear dynamics of H_2^+ and D_2^+ molecular ions were numerically studied. Despite these preliminary results, to our knowledge, quantum chemical studies describing the electronic structure of many-body systems based on the calculus of arbitrary-order have been scarce. The

present perspective aims to fill this gap in literature through the fractional generalization of some of the existing quantum chemical methods and presenting possible future directions for the advancement of fractional quantum chemistry. Following the common practice in literature, we adopt the names fractional calculus and calculus of arbitrary-order, interchangeably. However, whenever possible, the latter should be preferred for mathematical rigor.

The present perspective is organized as follows: Section II briefly overviews the historical and fundamental aspects of fractional calculus. In Sec. III, various types of FSE alongside their mathematical properties and physical applications are discussed. Section IV focuses on two important controversial topics and open problems that are the major sources of long-standing confusions in literature. Next, some potential areas of the applications of fractional calculus in quantum chemistry such as the fractional generalization of the self-consistent field (SCF) methods, fundamental molecular integrals and electron correlation energy, are presented in Sec. V. The description of dynamic-order nonlocal effects within the framework of variable-order fractional calculus is discussed in Sec. VI. Possible avenues for the future applications of the calculus of arbitrary-order in quantum chemistry are outlined in Sec. VII.

II. Calculus of Arbitrary-Order

The history of fractional calculus is as old as its classical Newtonian counterpart dating back to L'Hôpital's 1695 letter to Leibniz raising the possibility of extending the integer-order derivatives to their fractional variants (For a comprehensive historical survey, see Refs. 8, 20, and 21). Despite many contributions from eminent mathematicians such as Bernoulli, Laplace, Fourier and others, the calculus of arbitrary-order remained a subject of pure mathematical interest for centuries until a few decades ago, where it started garnering attention from researchers in engineering, physics, biology, and applied mathematics.⁸ In 1823, Abel published his landmark paper^{22,23} on tautochrone problem where he introduced RL fractional integrals and Caputo fractional derivatives which are still the most widely used forms of fractional operators. The RL fractional integral can be considered as a generalization of Cauchy's integral formula for n -fold repeated integration,

$$I^n[f(x)] = \int_a^{x_n} \int_a^{x_{n-1}} \cdots \int_a^{x_1} f(x_0) dx_0 \cdots dx_{n-1} = \frac{1}{(n-1)!} \int_a^x (x-\xi)^{n-1} f(\xi) d\xi, \quad (1)$$

to its non-integer-order forms, defined as

$${}^{\text{RL}}_a I_x^\alpha[f(x)] = \frac{1}{\Gamma(\alpha)} \int_a^x (x-\xi)^{\alpha-1} f(\xi) d\xi, \quad \text{and} \quad (2a)$$

$${}^{\text{RL}}_x I_b^\alpha[f(x)] = \frac{1}{\Gamma(\alpha)} \int_x^b (\xi-x)^{\alpha-1} f(\xi) d\xi, \quad (2b)$$

where $-\infty < a < x < b < \infty$ and the function f is Lebesgue-integrable on the open interval (a, b) or $f \in L^1(a, b)$. Here, $\Gamma(\alpha)$ is the Euler Gamma function and $\text{Re}(\alpha) > 0$. The domain of Lévy index α can also be extended to the set of complex numbers ($\alpha \in \mathbb{C}$) through analytic continuation. Equations 2a and 2b define the left- and right-sided RL fractional integral operators, respectively, which can also be viewed as the left-inverse of the corresponding fractional derivatives. As such, the factorization of fractional derivative operator as

$$\begin{aligned} D^\alpha &= (\pm 1)^m D^m D^{\alpha-m} \\ &= (\pm 1)^m \left(\frac{d^m}{dx^m} \right) I^{m-\alpha}, \quad \text{where} \quad m \in \mathbb{N}, \end{aligned} \quad (3)$$

allows for the interpretation of the fractional derivative operator as an ordinary derivative preceded by a fractional integral, if a concrete definition for the latter is provided. In Eq. 3, \mathbb{N} denotes the set of natural numbers, and the positive and negative signs correspond to the left- and right-sided fractional operators, respectively. Note that the equality of $I^\alpha = D^{-\alpha}$ is also assumed. Adopting RL fractional integral operators, for example, one can define the left- and right-sided RL fractional derivative operators as

$${}^{\text{RL}}_a D_x^\alpha [f(x)] = \left(\frac{d^m}{dx^m} \right) {}^{\text{RL}}_a I_x^{m-\alpha} [f(x)], \quad x \in \mathbb{R}, \quad \text{and} \quad (4a)$$

$${}^{\text{RL}}_x D_b^\alpha [f(x)] = (-1)^m \left(\frac{d^m}{dx^m} \right) {}^{\text{RL}}_x I_b^{m-\alpha} [f(x)], \quad x \in \mathbb{R}, \quad (4b)$$

respectively, where $m - 1 < \alpha \leq m$ and \mathbb{R} stands for the set of real numbers. For $\alpha = 0$, both RL integrals become identity operators. Setting $a = 0$ (or $b = 0$) in the left- (or right-) sided RL fractional derivatives in Eq. 4a (or Eq. 4b), yields Riemann's definition of the fractional derivatives. By allowing $a \rightarrow -\infty$ (or $b \rightarrow +\infty$) instead, one obtains Liouville's interpretation of the fractional derivatives. As an example, the Riemann fractional derivative of $f(x) = x^n$ can be written as

$${}^{\text{RL}}_0 D_x^\alpha [f(x)] = \left[\frac{\Gamma(n+1)}{\Gamma(n-\alpha+1)} \right] x^{n-\alpha}, \quad (5)$$

which is a generalization of the integer-order derivative expression for the power functions where factorials are replaced by the Gamma functions. Note that the right-hand side of Eq. 5 can also be obtained from other types of fractional derivatives of the power function. Plots of the Riemann derivative of the quadratic function, calculated on the positive side of the real axis ($x > 0$), are illustrated in Fig. 1. Here, the differentiation order of $\alpha \in [0, 2]$ and the step size of $\Delta\alpha = 0.1$ are adopted.

Figure 1 demonstrates that the Riemann fractional derivative of the power function can smoothly interpolate between its integer-order derivative counterparts. Equation 5 reveals an important distinction between fractional and conventional derivatives: the Riemann (and more generally, the RL) fractional derivatives of a constant (*e.g.*, x^0 when $x \neq 0$) can be non-zero.⁸

Interchanging the order of differentiation and integration in Eq. 3 yields the definition of the Caputo derivative operators, written as

$${}^{\text{C}}_a D_x^\alpha [f(x)] = \frac{1}{\Gamma(m-\alpha)} \int_a^x (x-\xi)^{m-\alpha-1} \left(\frac{d^m f(\xi)}{d\xi^m} \right) d\xi, \quad \text{and} \quad (6a)$$

$${}^{\text{C}}_x D_b^\alpha [f(x)] = \frac{(-1)^m}{\Gamma(m-\alpha)} \int_x^b (\xi-x)^{m-\alpha-1} \left(\frac{d^m f(\xi)}{d\xi^m} \right) d\xi, \quad (6b)$$

where $m - 1 < \alpha \leq m$ and the function f belongs to the set of absolutely m -continuous functions on the closed interval $[a, b]$ or $f \in AC^m[a, b]$. The condition $f^{(m)} \in L^1(a, b)$ is also assumed for interchanging the order of differentiation and integration in Eq. 3. Equations 6a and 6b imply that contrary to the RL derivatives (Eqs. 4a and 4b), the Caputo fractional derivatives of a constant are equal to zero.

III. Fractional Schrödinger Equation

Brownian paths are an important example of fractals in physics—self-similar and non-differentiable trajectories with fractal dimensions distinct from their topological dimensions. Feynman's path

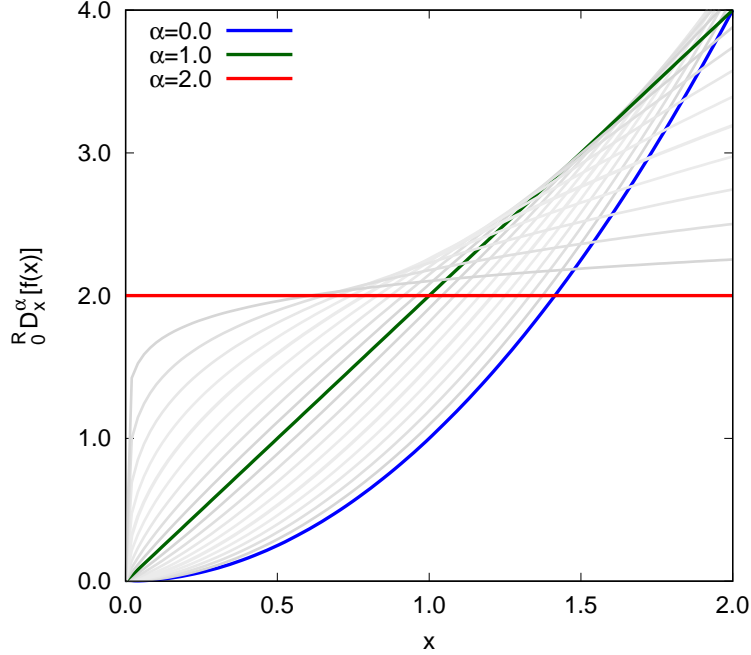


FIG. 1: The left-sided Riemann fractional derivative of the quadratic function, $f(x) = x^2$, where $\alpha \in [0, 2]$ and $x > 0$. Plots of fractional derivatives of arbitrary-order (grey) coincide with those of integer-order differentiation for $\alpha = 0.0$ (blue), $\alpha = 1.0$ (green), and $\alpha = 2.0$ (red). A step size of $\Delta\alpha = 0.1$ is adopted for illustration.

integral over Brownian trajectories not only provides an independent realization of non-relativistic Schrödinger equation but also signifies the first successful interpretation of fractional dimensions in quantum mechanics.²⁴ Inspired by Feynman's work, Laskin adopted the path integrals over Lévy flights and formulated the space-FSE,²⁵ which can be written as

$$i\hbar\partial_t\Psi(\mathbf{r},t) = \hat{H}_\alpha\Psi(\mathbf{r},t), \quad (7)$$

where \hbar is the Planck constant, ∂_t denotes ordinary differentiation with respect to time and \hat{H}_α is the fractional Hamiltonian operator defined as

$$\hat{H}_\alpha = D_\alpha(-\hbar^2\Delta)^{\alpha/2} + \hat{V}(\mathbf{r}), \quad 1 < \alpha \leq 2. \quad (8)$$

Here, Δ is the Laplacian operator, D_α represents the scale coefficient of dimension $[D_\alpha] = [\text{energy}]^{1-\alpha} \times [\text{length}]^\alpha \times [\text{time}]^{-\alpha}$, $\hat{V}(\mathbf{r})$ is the potential operator, and $\Psi(\mathbf{r},t)$ is the time-dependent wave function with temporal, t , and spatial coordinates, \mathbf{r} , respectively. Note that the α -stable Lévy distributions with Lévy index α , where $0 < \alpha \leq 2$, have finite moments of order $\mu < \alpha$ and infinite moments for higher orders. However, the existence of first-order moments such as position, $\langle x \rangle$, and momentum, $\langle p \rangle$, expectation values restricts the Lévy index to $1 < \alpha \leq 2$.²⁵ For $\alpha = 2$, Lévy and Gaussian distributions are equal and moments of all orders become stable. Simultaneously, $D_2 = 1/(2m_e)$, where m_e is the mass of electron, and H_α reduces to its conventional form. Laskin's derivation of space-FSE was based upon the Fourier integral transform representation of the quantum Riesz fractional derivative operator, $(-\hbar^2\Delta)^{\alpha/2}$, defined as

$$(-\hbar^2\Delta)^{\alpha/2}\Psi(\mathbf{r},t) = \frac{1}{(2\pi\hbar)^3} \int |\mathbf{p}|^\alpha e^{\frac{i\mathbf{p}\cdot\mathbf{r}}{\hbar}} \Phi(\mathbf{p},t) d^3p, \quad (9)$$

where \mathbf{p} is the momentum. Here, the wave function representations in configuration, $\Psi(\mathbf{r}, t)$, and momentum, $\Phi(\mathbf{p}, t)$, spaces are related to each other through 3-dimensional Fourier transformations given by

$$\Psi(\mathbf{r}, t) = \frac{1}{(2\pi\hbar)^3} \int e^{\frac{i\mathbf{p}\cdot\mathbf{r}}{\hbar}} \Phi(\mathbf{p}, t) d^3p, \quad \text{and} \quad \Phi(\mathbf{p}, t) = \int e^{\frac{-i\mathbf{p}\cdot\mathbf{r}}{\hbar}} \Psi(\mathbf{r}, t) d^3r. \quad (10)$$

Based on the similarities between diffusion and Schrödinger equations, Naber adopted the Caputo fractional derivative operator for the time variable to formulate the time-FSE.²⁶ In contrast to space-FSE, the Hamiltonian in time-FSE is non-Hermitian and nonlocal in time. As such, the resulting wave functions are not invariant under time reversal and probabilities are not be conserved. Furthermore, the solutions to the time-FSE for free particle and infinite potential well models revealed that probabilities and energy levels increase with time to a limiting value which depends on the fractional order of differentiation with respect to time.²⁶ Later, different variants of space-time FSE were developed, in which fractional derivatives of both space and time variables were employed.^{27,28}

IV. Controversies and Open Problems

An unfortunate reality about the calculus of arbitrary-order is the existence of multitudes of definitions for fractional operators.⁸ Furthermore, there are different sets of criteria^{20,29,30} for categorizing an integral or differential operator as fractional, some of which are still subject of ongoing debates.^{29,30} For example, the *law of exponents* or *index law* raises the “the philosophical controversy” on whether each criterion should correspond to the fractional operator or its operand.^{29,31} Moreover, Tarasov showed that linear derivative operators of non-integer order cannot satisfy Leibniz’s rule or otherwise, should be crossed out from the list of fractional derivatives.³² Tarasov’s theorem affects many derivative operators in literature that were previously considered as fractional.

The inconsistent treatment of fractional operators combined with the rapid growth of their applications in a variety of research areas in science and engineering has littered the literature with confusion and controversy. For example, Jeng *et al.*³³ demonstrated that piecewise continuous solutions to space-FSE with model potentials such as infinite potential well cannot be valid due to the nonlocal nature of the fractional differential operators. These results were later corroborated by Luchko who reformulated the problem in terms of integral equations with power kernels.³⁴ Bayın presented a different view of this problem³⁵ opposing the results of Refs. 33 and 34. Hawkins and Schwarz³⁶ pointed out an error in Bayın’s methodology, thereby reaffirming the original results of Ref. 33. Several authors^{37–39} adopted various types of fractional derivatives such as Weyl³⁸ and Caputo-Fabrizio³⁹ to analyze the solutions of FSE for the one-dimensional infinite potential well, again, in a piecewise continuous fashion. As such, the aforementioned controversies cast doubt on the existing results in literature making it imperative for the quantum chemistry community to be aware of such pitfalls and open problems while advancing the development of fractional quantum chemical models from a firm mathematical standpoint.

V. Applications

Calculus of arbitrary-order is a powerful tool to study the nonlocal aspects of electron correlation, such as memory and long-range effects, in strongly correlated systems. The majority of

theoretical studies in this area, including the applications of FSE, are mainly focused on simple model systems.^{33–38,40,41} However, to our knowledge, the realization of fractional quantum chemical models based on space-, time- and space-time-FSE is still lacking. As such, at least two methods for the generalization of non-relativistic time-independent methods to the fractional regime can be envisioned: The substitution of either (i) the Laplacian operator in the kinetic term, and/or (ii) the Coulomb operator in the potential term with their fractional counterparts. Despite Laskin’s formulation of FSE in Gaussian-cgs unit system (Eqs. 7–10), we adopt Hartree atomic units (a.u.) to develop our fractional quantum chemical models throughout the remaining parts of this manuscript.

A. Fractional self-consistent field methods

The Hartree-Fock (HF) method is one of the pillars of modern electronic structure theory which plays a central role in quantum chemistry. It delineates the electronic structure of an N -electron system by focusing on the interactions of individual electrons with an effective potential generated by the remaining $N - 1$ electrons in an average sense. Thus, Coulomb electron correlation effects are absent in the HF theory, by construction. However, the fractional realization of the HF method offers new insights into the electronic structure of many-body systems through capturing nonlocal correlation effects. An expedient way towards fractional generalization of the HF method is to replace the Laplacian operator in the kinetic energy term with its quantum Riesz fractional derivative counterpart. Let the N -electron HF wave function, $|\Psi\rangle$, be represented by an antisymmetric product (Slater determinant) of spin-orbitals, $\chi(\mathbf{x})$, where $\{\chi_j(\mathbf{x})|j = 1, 2, 3, \dots, N\}$ and \mathbf{x} collectively stands for the spatial and spin coordinates of an electron. Using Slater-Condon rules,² the fractional ground-state energy, E_0^α , of a single-determinant wave function can be written as

$$E_0^\alpha = \langle \Psi_0 | \hat{H}_\alpha | \Psi_0 \rangle = \sum_{j=1}^N \langle j | \hat{h}_\alpha | j \rangle + \frac{1}{2} \sum_{j=1}^N \sum_{k=1}^N \langle jk || jk \rangle, \quad (11)$$

in which, the expectation value of the fractional core-Hamiltonian, \hat{h}_α , and the element of anti-symmetric two-electron-repulsion integral tensor, $\langle jk || jk \rangle$, are defined as

$$\langle j | \hat{h}_\alpha | j \rangle = \int \chi_j^*(\mathbf{x}) \left[\bar{D}_\alpha (-\Delta)^{\alpha/2} - \sum_A \frac{Z_A}{r_A} \right] \chi_j(\mathbf{x}) d\mathbf{x}, \quad \text{and} \quad (12)$$

$$\langle jk || jk \rangle = \iint \chi_j^*(\mathbf{x}_1) \chi_k^*(\mathbf{x}_2) r_{12}^{-1} (1 - \hat{\mathcal{P}}_{12}) \chi_j(\mathbf{x}_1) \chi_k(\mathbf{x}_2) d\mathbf{x}_1 d\mathbf{x}_2, \quad (13)$$

respectively. Here, \bar{D}_α is the scale coefficient in a.u., the asterisk denotes complex conjugation, $\hat{\mathcal{P}}_{12}$ is the permutation operator, r_{12} is the interelectronic distance and r_A is the distance of an electron from the nuclear center A of charge Z_A . The minimization of the fractional energy functional, $E^\alpha[\chi(\mathbf{x})]$, with respect to the variations of spin-orbitals, subject to their orthonormality, yields the set of fractional Riesz-Hartree-Fock equations in their integro-differential form, which after transformation to the canonical set of spin-orbitals, can be written as

$$\left[\hat{h}_\alpha + \sum_{k=1}^N \langle \chi_k | r_{12}^{-1} (1 - \hat{\mathcal{P}}_{12}) | \chi_k \rangle \right] |\chi_j\rangle = \epsilon_j^\alpha |\chi_j\rangle, \quad j = 1, 2, 3, \dots, N. \quad (14)$$

The expression within the brackets in Eq. 14 defines the fractional Fock operator, \hat{f}_α . The second and third terms in the Fock operator are Coulomb and exchange potentials, which collectively

define the HF effective potential operator, $\hat{v}_{\text{HF}}(\mathbf{r})$. Due to the dependency of the HF potential on the spin-orbitals, solutions to the system of Eqs. 14 are often obtained through an iterative SCF procedure within a generalized matrix eigenvalue form represented in a finite set of basis functions. The resulting eigenvalue expression is called Roothan-Hall or Pople-Nesbet equation, depending on whether or not the spin symmetry restrictions are imposed on the basis functions, respectively.² The derivation of fractional Kohn-Sham (KS) equations is similar to the aforementioned process for the derivation of the fractional HF method. However, it requires a generalized form for fractional noninteracting kinetic energy density functional similar to the one proposed in Eq. 12.

In addition to the kinetic energy operator, both classical Coulomb and exchange-correlation potentials can also be extended to the fractional regime. For the former, convolution integrals with fractional weight factors, $r^{-\alpha} = |\mathbf{r}_1 - \mathbf{r}_2|^{-\alpha}$, were used in the context of nuclear and cluster physics and folded potentials where the variation of fractional index α allowed for a smooth interpolation between Coulomb and Yukawa type potentials.⁷ Furthermore, a combination of Mie-type potentials and Jumarie-type derivative operator for the kinetic term were also employed to study the energy spectrum of a typical diatomic molecule by investigating the solutions of FSE in a N -dimensional hyperspherical coordinate system.⁴²

Although in the fractional generalization of HF (and KS) equations, the Riesz derivative operator was adopted, other types of fractional operators can also be used if they do not violate the quantum mechanical principles and mathematical requirements within their domain of definitions. As such, the unification methods such as fractional corresponding operators⁴³ or generalized fractional operators⁸ can be employed to ensure a unified and consistent realization of fractional models which are independent of the specific choice of fractional operators. The fractional corresponding operators offer an additional nice feature that their pertinent FSEs are derivable from path integrals over Lévy flights.⁴³ The RL, Caputo, Riesz and Grünwald-Letnikov operators are examples of fractional corresponding operators.

B. Fundamental fractional molecular integrals

In the standard formulation of quantum chemistry, the fundamental kinetic energy molecular integrals over Gaussian-type orbitals (GTOs) are expressed as⁴⁴

$$I_K = \int e^{-\gamma|\mathbf{r}-\mathbf{A}|^2} \left[-\frac{1}{2}\Delta_{\mathbf{r}} \right] e^{-\zeta|\mathbf{r}-\mathbf{B}|^2} d\mathbf{r}, \quad (15)$$

where the exponents γ and ζ are positive real numbers and the Laplacian operator carries the differentiation with respect to the spatial variable \mathbf{r} . Equivalently, the differentiation can also be performed with respect to the nuclear coordinate \mathbf{B} as

$$I_K = -\frac{1}{2} \left[\frac{\partial^2}{\partial B_x^2} + \frac{\partial^2}{\partial B_y^2} + \frac{\partial^2}{\partial B_z^2} \right] I_S, \quad (16)$$

where I_S denotes the overlap integral between two GTOs. Thus, the task of computing the fundamental kinetic energy integrals over GTOs can be reduced to the calculation of overlap integrals and their derivatives with respect to the nuclear coordinates.⁴⁴ What makes fractional HF or KS-DFT methods different from their conventional counterparts is the substitution of the kinetic energy derivative or potential integral operators with their fractional variants. Therefore, the fundamental fractional kinetic energy integrals over GTOs can be written in their general form as

$$I_K^\alpha := \int e^{-\gamma|\mathbf{r}-\mathbf{A}|^2} \left[\bar{D}_\alpha (-i)^\alpha \hat{T}_\alpha \right] e^{-\zeta|\mathbf{r}-\mathbf{B}|^2} d\mathbf{r}, \quad (17)$$

where \hat{T}_α is the generalized^{7,8,30} or the corresponding fractional differential operator.⁴³ The matrix elements of fractional kinetic operators should be calculated once for each value of α and remain constant during the course of SCF procedure. However, the mathematical convenience in computing the fundamental kinetic energy integrals as operator expressions⁴⁵ in terms of overlap integrals and derivatives with respect to the nuclear coordinates might not necessarily exist for the fractional kinetic energy operators. Therefore, mathematical techniques such as Euler integral transforms of elementary functions expressed as generalized hypergeometric functions with power-law arguments⁴⁶ can alternatively be employed to facilitate the derivation of working expressions for the fundamental integrals. The treatment of the fundamental molecular integrals of electron-nuclear attraction and electron-electron repulsion potentials, where the (anti-)Coulomb operator is replaced by its fractional tensor operator counterpart, requires a much more detailed approach^{7,42,45} which is out of the scope of this manuscript and will be presented elsewhere.

C. Fractional electron correlation energy

The classical definition of the electron correlation energy¹ can be extended to its fractional form as

$$E_c^\alpha := \mathcal{E} - E_{\text{HF}}^\alpha, \quad (18)$$

where \mathcal{E} is the exact non-relativistic energy and E_{HF}^α stands for fractional HF energy calculated in the limit of complete-basis set with fractional Lévy index α . In practice, however, one often resorts to the concept of *basis-set correlation energy* described in Ref. 2. Note that when the fractional Lévy index changes, the order of fractional kinetic operator and the corresponding integro-differential equation vary as well. Hence, the resulting set of eigenvalues and eigenfunctions of the fractional HF equations (if exist) will change accordingly.

Another useful metric to measure the improvement in the description of correlation energy, due to the incorporation of fractional nonlocalities in the model, can be defined as

$$\Delta E_c^\alpha := E_c - E_c^\alpha = -(E_{\text{HF}} - E_{\text{HF}}^\alpha). \quad (19)$$

It is important to note that Eq. 18 is mathematically ambiguous (similar to its conventional form) because it does not specify which type of fractional operator is adopted for the generalization of the HF model. Also, Eq. 19 implies that a fractional model becomes most useful in practice if it is able to reproduce the classical results when Lévy index takes integer values. For example, both problems can be addressed in the Riesz-Hartree-Fock method where E_c and E_{HF} , respectively, represent the correlation and HF energies (corresponding to $\alpha = 2$) and E_c^α and E_{HF}^α are their fractional counterparts (pertinent to $1 < \alpha < 2$).

VI. Variable-Order Fractional Calculus

Compared with the long history of constant-order fractional calculus, the fundamental theory of variable-order fractional calculus was not fully developed until 1993.⁴⁷ Later, the theoretical foundations of variable-order fractional differential equations alongside the existence and uniqueness of their solutions^{48–52} were established by several authors.⁵³ Despite the growing number of applications of the variable-order fractional calculus in various branches of science and engineering,^{8,31,47,54} particularly, recent numerical studies on the solutions to the specific classes of variable-order

FSE,^{55–58} to our knowledge, there has been no study in the literature focusing on the electron correlation problem.

As previously mentioned, the constant-order fractional operators can describe the *static-order* nonlocal correlation effects in the electronic structure of many-body systems.⁵⁹ Nevertheless, when the nature of the quantum nonlocal effects dynamically evolve, the constant orders of differentiation or integration, α , should be replaced with a dependent variable, $\alpha(\cdot)$. Thus, both memory effects and long-range electron correlation not only become associated with the inherent nonlocal nature of the fractional operators (fading memory),³¹ but also the functional form of the variable order itself (order memory).^{6,31,60} For example, a study on the reaction kinetics of the proteins suggests that the fractional order of the relaxation mechanism depends on temperature.⁶¹ Therefore, variable-order fractional operators can be adopted to describe the *dynamic-order* nonlocal effects pertinent to the evolving nature of the relation between the relaxation mechanism of the proteins and the temperature. Recently, different ansätze of the general form, $\alpha(t, \tau) := \alpha(At + B\tau)$,^{6,31,60} have been proposed for the variable order of fractional integro-differential operators including: case (1), $\alpha(t, \tau) := \alpha(t)$; case (2), $\alpha(t, \tau) := \alpha(\tau)$; and case (3), $\alpha(t, \tau) := \alpha(t - \tau)$. Here, A and B are constants, t is an independent variable and τ is the dummy variable in the integral representation of the fractional operator. It has been demonstrated^{6,31,60} that the rate of response from fractional operators is inversely proportional to the variations in the order memory such that case (1) exhibits no memory, case (2) indicates a weak memory and case (3) displays a strong memory of the history of the order variations.^{6,31,60}

VII. Outlook

The realization of fractional quantum chemistry opens the doors to a pristine area of research in molecular physics and offers new insights into the delineation of the electronic structure of the complex electronic environments. The fractional integro-differential operators of constant- and variable-order can be adopted to describe the static- and dynamic-order quantum nonlocalities such as memory effects and long-range electron correlation in the strongly correlated systems. There is a mounting body of evidence in literature demonstrating the generality and superior performance of the space-, time- and space-time variants of FSE compared with their classical counterparts for complex electronic systems with dominant nonlocal effects of fractional nature. The rapid growth of the applications of FSE in different branches of physics, notwithstanding was not without side-effects: The existence of multiple sets of criteria and definitions for fractional operators combined with inconsistent mathematical interpretations have littered the literature with numerous controversies and confusions.

Following the development of various classes of FSE in quantum mechanics, the present perspective mainly focuses on the generalization of the existing quantum chemical models such as HF and KS-DFT to their fractional versions. As such, necessary ingredients such as fundamental molecular integrals of fractional operators and concepts such as the correlation energy have been extended to their fractional variants. An important area for future investigations involves the numerical techniques of constant- and variable-order fractional calculus of variation and their applications in the development of fractional quantum chemistry. To our knowledge, within the quantum chemistry community,^{55–58,62} very little is known about the stability, convergence rate and computational scaling of the constant- and variable-order fractional methods. Therefore, the understanding of the mathematical aspects of fractional numerical techniques^{8,59,63,64} is of key importance for the development of fractional models in quantum chemistry.

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