FULL PAPER



CHEMISTRY WILEY

Introducing the γ function in quantum theory

Revised: 4 January 2020

Péter R. Surján 💿

Laboratory of Theoretical Chemistry, Institute of Chemistry, Faculty of Science, ELTE Eötvös Loránd University, Budapest, Hungary

Correspondence

Péter R. Surján, Laboratory of Theoretical Chemistry, Institute of Chemistry, Faculty of Science, ELTE Eötvös Loránd University, H-1518, Budapest 112, P.O.B. 32, Hungary. Email: surjan@chem.elte.hu

Funding information

ELTE Excellence Program supported by the Hungarian Ministry of Human Capacities, Grant/Award Number: 783-3/2018/ FEKUTSRAT; Nemzeti Kutatási Fejlesztési és Innovációs Hivatal, Grant/Award Number: NKFIH-K115744

Abstract

Through a series of postulates, we define a function $\gamma(x)$ whose square acts as Dirac's $\delta(x)$ and exhibits several unusual properties. Though the square root of δ cannot be defined among distributions, it appears in quantum theory if one wants to associate a wave function to a (quasi)classical particle having charge distribution $\delta(x)$. The newly defined function $\gamma(x)$ serves to describe quasi-classical particles using part of the quantum formalism (eg, wave functions, operators, expectation values) but exhibiting classical properties. The function $\gamma(x)$ appears to be useful to define model wave functions for simple (quasi)quantum systems. In a spherical coordinate system, $\gamma(r - r_0)$ leads to a quasi-classical "bubble" model of the hydrogen atom, where the electron is distributed on the surface of a sphere with radius r_0 , and it provides exact quantum mechanical energies of its total symmetric levels. For other simple quantum systems, it provides approximate but meaningful energies. In particular, exact energy differences for harmonic oscillator levels are obtained, with the zero-point energy missing.

KEYWORDS

harmonic oscillator, hydrogen atom, quasiclassical mechanics, square-root of Dirac's delta

1 | INTRODUCTION

The success of current quantum chemistry is impressive. Chemical systems of relatively large size are available for calculations with chemical accuracy,^[1-3] and small systems (up to a few atoms) can be treated theoretically up to the precision of high-resolution spectroscopy.^[4,5] This success is partly due to the fast development in computer technology, but also due to the elaboration of powerful theoretical methods.^[6,7]

Although further development in the above areas can be expected, a common problem of virtually all theoretical approaches is that they require computations that scale badly with the system size. Most accurate methods scale exponentially, but others with the fourth, sixth, or eighth power of the system size.^[6,7] Fragmentation methods and linear scaling technologies show a very promising development,^[8–14] but even these require certain compromise between speed and accuracy.

In this situation, there appears to be a need for simple and qualitative models that cannot compete with calculations with quantitative accuracy but may reveal some essential features of quantum chemical phenomena. One possibility to develop such models is to use semiempirical techniques adapted to current needs. These have indeed proven to be useful in describing complex systems.^[13,15-21]

A completely different direction to develop useful models for quantum systems may come from semiclassical theory. This field has already been widely studied,^[22-24] but its application to quantum chemistry^[25,26] is not yet fully explored, with the exception of atomic

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2020 The Author. International Journal of Quantum Chemistry published by Wiley Periodicals, Inc.

^{2 of 12} WILEY CHEMISTRY

and molecular scattering theory where it constitutes a common methodology.^[24,27-31] The success of quasi-classical treatment in this latter field may hint that applications in other areas may also prove useful—this is just envisioned in this paper. In fact, there exist phenomena that generate severe complications for quantum chemical methods, but they do appear also in classical mechanics—interparticle correlation, for example. We feel that studying semiclassical theories may induce a new thread of theoretical developments with chemical applications.

Several models and mathematical approaches exist bridging classical and quantum mechanics. One may mention the seminal Bohr model,^[32] expansions in terms of \hbar like the Wentzel–Kramers–Brillouin (WKB) approximation,^[33,34] or the limit of large quantum numbers.

In this paper we sketch a rather different idea, taking an initial step to develop a quantum mechanical (QM) formalism capable of treating quasi-classical particles. This will require us to introduce a new "function" of the coordinate that we denote by $\gamma(x)$, which, in some sense, can be considered the square root of Dirac's $\delta(x)$.

Introduction of $\gamma(x)$ as presented here is rather intuitive, as had been the first introduction of Dirac's δ . The latter has been subsequently clarified by the distribution theory of Schwartz.^[35,36] However, in distribution theory one has the so-called Schwartz's impossibility theorem^[37] stating that no distributive multiplication, hence no powers or hence no fractional powers (consequently no square roots), can be defined for distributions. The "square root" of Dirac's δ , therefore, should be validated in a different, perhaps yet unknown mathematical framework. Until this validation takes place, we shall follow an intuitive definition of $\gamma(x)$ defining its basic properties as "postulates." The argument in favor of using the intuitively introduced function $\gamma(x)$ is merely its applicability for actual problems, some of them being presented in this paper.

The rest of the article is organized as follows. First, the motivation behind introducing the function γ is given, followed by the postulates it should satisfy. The basic properties of γ and the calculus for its use are presented subsequently. Then the treatment of the H atom, the harmonic oscillator, and the He atom are given as examples. The paper is closed by a discussion of the results and of some features and perspectives of γ .

This paper is intended to be the first of a series exploiting the use of the γ function in quantum chemistry. In subsequent papers, the physical origin of $\gamma(x)$ and its further mathematical properties will be investigated. We also expect to present novel results on many-electron systems or inherently quasi-classical systems: a quantum dot, for example. Investigating the physical origin of function γ is connected to studying the behavior of quantum motions near the classical turning point, and we hope that these studies will explain why the examples presented in this paper for the H atom and for the harmonic oscillator work so well. Mathematical problems associated with the function γ , some of them mentioned in the text below, have to be studied in more detail. Further applications must clarify the field of application of $\gamma(x)$ as a wave function, separating the systems for which it works well from those for which acceptable approximate results can be expected, and finally from those where it is inappropriate.

2 | THE γ FUNCTION

Consider a classical point-like particle with unit charge at point r₀ having charge density

$$\rho(\mathbf{r}) = \delta(\mathbf{r} - \mathbf{r}_0).$$

This generates the electrostatic potential $1/|r - r_0|$ via Poisson's equation. If one wishes to associate a wave function to this particle, one may write

$$\psi(r) = \sqrt{\rho(r)} = \delta^{1/2}(r - r_0).$$

This satisfies the fundamental quantum mechanical requirement that $|\psi|^2 = \rho$. Unfortunately, as mentioned in Introduction, $\delta^{1/2}(r)$ does not exist either among common functions or among distributions (generalizations of distribution theory such as Colombeau algebra^[38,39] are not considered here). We shall avoid using the notation $\delta^{1/2}$ but proceed differently.

2.1 | The axioms of γ

As mentioned above, the square root of $\delta(x)$ is undefined. Nevertheless, the existence of a generalized function γ is postulated with the following axioms:

$$\gamma(x-x_0) = 0 \text{ for } x \neq x_0$$
 (1a)

CHEMISTRY-WILEY 3 of 12

$$\int_{-\infty}^{\infty} \gamma^2(x - x_0) f(x) \, dx = f(x_0)$$
(1b)

$$\int_{-\infty}^{\infty} \gamma(x) f(x) \gamma''(x) dx = 0, \qquad (1c)$$

the prime indicating the derivative, for virtually arbitrary functions f(x). Integration over x can denote one- or three-dimensional integration depending on the problem in question.

The first two axioms of γ reflect our wish to associate its square to δ . The last axiom Equation (1c) will be termed as the "kinetic postulate" for reasons explained below.

As for Dirac's δ , it would be tempting to present a function series, which, in the infinite limit of some parameter they contain, tend to $\gamma(x)$ satisfying all the above axioms. Work to find such a series is in progress, and we hope to present some results in subsequent papers. However, this task is rather nontrivial. For instance, consider the case of the usual δ -series approaching $\delta(x)$:

$$\delta(x) = \lim_{\epsilon \to \pm 0} \frac{1}{\sqrt{\pi\epsilon}} e^{-x^2/\epsilon}.$$

This representation of the delta function ensures that in the limit $\delta(x)$ is zero almost everywhere, but it is singular at x = 0, and due to the proper normalization one has the integral

$$\int_{-\infty}^{\infty} \delta(x) \, dx = 1$$

ensuring the basic property of $\delta(x)$ for any well-behaved function f(x)

$$\int_{-\infty}^{\infty} f(x)\delta(x) \, dx = f(0)$$

which makes it possible to define $\delta(x)$ as a continuous linear functional, that is, a distribution.

If one tries to define $\gamma(x)$ as the limit of the square roots of the terms of the delta series, that is, one tries to define $\gamma(x)$ as

$$\lim_{\epsilon \to +0} \frac{1}{4\sqrt{\pi\epsilon}} e^{-x^2/(2\epsilon)},$$

one realizes that this definition satisfies axioms Equations (1a) and (1b) but fails to satisfy axiom Equation (1c).

As can be checked, similar conclusions can be drawn by taking the square roots of the terms of other well-known delta-series before taking the limit. It remains to be seen whether a different special construction is possible to originate the gamma function in a similar way. The answer can be yes or no, but at the present stage the most important question is whether the three axioms of $\delta(x)$ are consistent. Although currently we cannot prove their mathematical consistency, no logical contradiction has been found between the axioms. This motivated us to publish this idea, hoping that someone from the scientific community will find a way to decide this question.

2.2 | Working with γ

To investigate whether a useful calculus with the function γ defined above can be set up, it is essential to require that usual mathematical rules apply. This is in analogy with the use of δ , where one requires, for example, that from its basic property

$$\int_{-\infty}^{\infty} \delta(x) f(x) dx = f(0)$$

the relations

WILEY-

4 of 12

$$\int_{-\infty}^{\infty} \delta^{(n)}(x) f(x) dx = (-1)^n f^{(n)}(0)$$
(2)

follow, the superscript (*n*) indicating *n*-times derivation. For $\delta(x)$, Equation (2) results from demanding that the rules of integration by parts are retained. In analogy, we require for the first derivative that

$$\int_{-\infty}^{\infty} (\gamma^2)'(x)f(x) \, dx = -f'(0).$$

Since $(\gamma^2)'(x) \equiv 2 \gamma(x) \gamma'(x)$, one finds the fundamental property of γ :

$$\int_{-\infty}^{\infty} \gamma(x) f(x)\gamma'(x) \, dx = -\frac{1}{2} f'(0). \tag{3}$$

Similarly, one may study higher derivatives, like

$$\int_{-\infty}^{\infty} (\gamma^2)^{(n)}(x) f(x) dx = (-1)^n f^{(n)}(0)$$

for the nth derivative. Upon integrating by parts as many times as necessary, one finds that

$$\int_{-\infty}^{\infty} \gamma(x) f^{(n-1)}(x) \gamma'(x) \, dx = -\frac{1}{2} f^{(n)}(0)$$

in consistence with Equation (3). It is interesting to observe that the integral

$$\int_{-\infty}^{\infty} \gamma(x) f(x) \gamma''(x) dx$$

which is postulated to be zero in Equation (1c), does not contribute to the above results. While the integral $\int \gamma f \gamma''$ shows up during the manipulations, it eventually drops out. An example for $\int \gamma f \gamma''$ being immaterial is given in the Appendix.

Recall that the "shape" of $\delta(x)$ and $\gamma(x)$ is the same: both are zero almost everywhere and singular at x = 0, their values being infinite. The difference between them is the strength of their singularities, measured by their integral. The latter is a finite value for $\delta(x)$, and of course for $\gamma(x)^2$. One may consider, however, the integral

$$\int_{-\infty}^{\infty} \gamma(x) f(x) dx = 0.$$

This could even be postulated, since such integrals will not appear in the examples studied here. We felt that this extra postulatum is unnecessary since, if the strength of the singularities of δ or γ^2 makes their integrals finite, it appears natural that the square root at the only nonzero value of the function is insufficient to produce a finite integral.

2.3 | Particle at rest

Axiom (1c), the "kinetic postulate", gets physical significance when evaluating the QM expectation value of the kinetic energy operator $\hat{T} = -\frac{1}{2}\frac{d^2}{dx^2}$ (atomic units are used throughout) with the wave function $\gamma(x)$:

$$\langle \hat{T} \rangle = -\frac{1}{2} \int_{-\infty}^{\infty} \gamma(x) \gamma''(x) dx = 0$$

Since this expression is 0 due to axiom Equation (1c), one can see that wave function $\gamma(x)$ describes a particle at rest at the origin. Similarly, $\gamma(x - x_0)$ is the wave function of a particle at x_0 . Clearly, this is a classical situation, which contradicts, for example, the Heisenberg uncertainty rule. Strict manifestation of this situation is possible only for (quasi)classical particles, a quantum dot for example. For this reason, the approach using γ for expressing a wave function is termed quasi-classical further on. This is not to be mixed with other uses of such a term, for example, the quasi-classical trajectory method where classical mechanics is used on potential surfaces obtained from quantum mechanics.

3 | HYDROGEN ATOM

3.1 | Ground state

A spherical model of the H atom emerges by considering the quasi-classical ground-state wave function

$$\Psi_{1s}(r) = \mathcal{N}\gamma(r-r_1)Y_{00}$$

in spherical coordinates, Y_{00} referring to the s-type spherical harmonics. The normalization constant is readily found to be $\mathcal{N} = 1/r_1$. This wave function corresponds to a model of the H atom in which the electron is distributed on the surface of a sphere with radius r_1 . On evaluating the potential energy of such an electron in the field of the proton providing the potential $\hat{V} = -1/r$, one gets in spherical coordinates

$$\langle \Psi_{1s}(r)|\hat{V}|\Psi_{1s}(r)\rangle = -\mathcal{N}^2 \int_0^\infty r^2 \gamma(r-r_1)\frac{1}{r} \gamma(r-r_1) dr$$

resulting in the classical electrostatic energy

$$\langle \Psi_{1s}(r)|\hat{V}|\Psi_{1s}(r)\rangle = -\frac{1}{r_1}.$$
 (4)

In evaluating the integral over r, axiom Equation (1b) was used.

Note that the function γ contributes to Equation (4) only through its square, δ . The situation is different for the expectation value of the kinetic energy \hat{T} :

$$\langle \Psi_{1s}(r)|\hat{T}|\Psi_{1s}(r)\rangle = -\frac{1}{2} \mathcal{N}^2 \int_0^\infty r^2 \gamma(r-r_1)\Delta \gamma(r-r_1) dr.$$

Since the wave function $\gamma(r - r_1)$ depends only on r, one needs only the radial part of the Laplacian

$$\Delta_r = \frac{2}{r} \frac{\partial}{\partial r} + \frac{\partial^2}{\partial r^2},$$

with $\hat{T} = -\frac{1}{2}\Delta_r$ in atomic units. Upon substituting the second term of the radial Laplacian, one gets zero due to the kinetic postulate Equation (1c). The first term, however, will contribute:

(5)

$$\langle \Psi_{1s}(r) | \hat{T} | \Psi_{1s}(r) \rangle = -\frac{1}{2} \frac{1}{r_1^2} \int_0^{\infty} r^2 \gamma(r - r_1) \frac{2}{r} \gamma'(r - r_1) dr$$

$$= -\frac{1}{r_1^2} \underbrace{\int_0^{\infty} \gamma(r - r_1) r \gamma'(r - r_1) dr}_{-\frac{1}{2}}$$

$$= \frac{1}{2r_1^2},$$

where in the last step we used the fundamental property Equation (3).

Adding Equation (4) to (5), the energy of the H atom is obtained in this model as a function of r_1 :

$$E(r_1) = \langle \Psi_{1s}(r) | \hat{T} + \hat{V} | \Psi_{1s}(r) \rangle = \frac{1}{2r_1^2} - \frac{1}{r_1}.$$

Minimizing this energy wrt r_1 , one gets $r_1 = 1$, the classical Bohr radius. At this value, the total energy is

$$E(r_1 = 1) = -\frac{1}{2},$$

which is the exact nonrelativistic energy of the ground state of H.

3.2 | Excited s states

Presence of orthogonal polynomials in the standard QM treatment of the H atom is essential to ensure the orthogonality of different states with the same angular quantum numbers. There is no such requirement in the quasi-classical model studied here, since $\gamma(r - r_1)$ and $\gamma(r - r_2)$ are automatically orthogonal for $r_1 \neq r_2$. Let us model the *n*th excited *s* state of the H atom with simple the Ansatz

$$\Psi_{ns} = \mathcal{N}_n r^{n-1} \gamma(r-r_n) Y_{00}, \quad n = 1, 2, 3, \dots$$
(6)

corresponding to distributing the electron on the surface of a sphere with radius r_n . The normalization constant becomes $N_n = 1/r_n^n$. For the potential energy, one gets

$$\langle \Psi_{ns} | \hat{V} | \Psi_{ns} \rangle = -\mathcal{N}^2 \int_0^\infty r^2 r^{2n-2} \gamma(r-r_n) \frac{1}{r} \gamma(r-r_n) dr$$

= $-\frac{1}{r_n}$, (7)

reflecting again classical electrostatics.

When evaluating the kinetic energy, in contrast to the 1s case, the term of the Laplacian containing second derivative wrt *r* also has a role. This is because, when taking the second derivative of $r^{n-1} \gamma(r - r_n)$, some terms contain only the first derivative of γ , and these terms do contribute via the fundamental property Equation (3). The term in which the second derivative of γ is present still does not contribute because of the kinetic postulate Equation (1c). The result for the kinetic energy expectation value is

$$\langle \Psi_{ns} | \hat{T} | \Psi_{ns} \rangle = \frac{n^2}{2r_n^2}$$

Thus the total energy of the *n*th state as a function of radius r_n is

$$E_n(r_n)=\frac{n^2}{2r_n^2}-\frac{1}{r_n}.$$

Minimizing this energy wrt r_n one gets $r_n = n^2$ as the optimal value, with the corresponding energies of the s states as

$$E_n = -\frac{1}{2} \frac{1}{n^2}$$

WILEY 7 of 12

which are the exact s-energies of the H atom.

One may wonder about the reliability of Ansatz Equation (6) to describe the radial function of *ns* states. Once we accept the "bubble" model distributing the electron on the sphere of radius r_n , only the radial factor r^{n-1} has to be discussed. As mentioned above, there is no need to include an orthogonal polynomial in front of γ to ensure the mutual orthogonality of *ns* states for different *n*, since the $\gamma(r - r_n)$ functions are automatically orthogonal for different radii r_n . Therefore, we have constructed Ansatz Equation (6) by selecting only the highest power of *r* of an orthogonal (Laguerre) polynomial. One may ask if this selection is arbitrary: for instance, an Ansatz $\sum_{j=0}^{n-1} c_j r^j$ would lead to different kinetic energy, making the present result arbitrary. The answer is no: using this trial wave function and optimizing all parameters c_j and r_n , one always gets the 1s energy as the wave function collapses to the 1s orbital. Further studies have to be carried out to see if, apart from the somewhat intuitive formula (6), where a simple power function is used to multiply $\gamma(r - r_n)$, some more complicated radial functions could be used with success.

3.3 | Nonspherical states

For the states $l \neq 0$, the quasi-classical model studied here is not exact any more since the degeneracy of *s*, *p*, *d*, ... states is lifted. Writing the wave function Ansatz as

$$\Psi_{nlm} = \mathcal{N}_n r^{n-1} \gamma(r-r_{nl}) Y_{lm}$$

provides the same result for the potential energy as in Equation (7), but for the expectation value of the kinetic term, the formula

$$\langle \hat{T} \rangle = \frac{n^2 + l(l+1)}{2r_{nl}^2}$$

is obtained, which depends on the azimuthal quantum number *I*. Minimizing the total energy wrt r_{nl} one gets

$$r_{nl} = n^2 + l(l+1)$$

providing the energy

$$E_{nl} = -\frac{1}{2} \frac{1}{n^2 + l(l+1)}$$

which is not the exact result, as it depends on *l*. This means that the Runge–Lenz symmetry^[40–42] is violated if the radial part of the wave function is modeled by the γ function.

4 | HARMONIC OSCILLATOR

Consider the Hamiltonian of the 1D oscillator in atomic units and with unit mass:

$$\hat{H} = -\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} \omega^2 x^2,$$

where ω is the angular frequency. Since the potential is an even function of *x*, one should use a symmetrized Ansatz for the *n*th quasi-classical state:

$$\Psi_n = \mathcal{N} x^n [\gamma(x - x_n) + \gamma(x + x_n)], n = 0, 1, 2, ...$$

For the normalization constant, one obtains

WILEY-

8 of 12

This wave function provides a rather crude model of the oscillator, enforcing the particle to be localized at $\pm x_n$ (the analogs of the classical turning points) in the *n*th quantum state. The kinetic energy integral, using axioms Equations (1a) to (1c) and the fundamental property Equation (3), becomes nonzero for $n \neq 0$:

$$\langle \Psi_n | -\frac{1}{2} \frac{d^2}{dx^2} | \Psi_n \rangle = \frac{n^2}{2x_n^2},$$

while the potential energy is simply

$$\langle \Psi_n | \frac{1}{2} \omega^2 x^2 | \Psi_n \rangle = \frac{1}{2} \omega^2 x_n^2$$

Minimizing the total energy

$$E_n(x_n) = \frac{1}{2} \left(\frac{n^2}{x_n^2} + \omega^2 x_n^2 \right)$$

wrt x_n , one gets for the optimal positions

$$x_n = \sqrt{\frac{n}{\omega}}$$

providing the optimal energy of the nth state as

 $E_n = n\omega$.

This is almost the exact QM result $(n + \frac{1}{2})\omega$ for the oscillator levels, the only difference being that the zero-point energy is absent from this quasi-classical description.

5 | THE HELIUM ATOM

In this paper, we focus on one-particle systems; the treatment of many-particle systems requires further studies. We report, however, an initial step, considering an oversimplified model of the He atom. The simplification partly matches the approach applied for the H atom: the two electrons of the helium will be distributed on the surface of a sphere of radius r_0 . A new type of simplification will be introduced below for describing interelectron repulsion. The Hamiltonian in atomic units is

$$\hat{H} = -\frac{1}{2}\Delta_1 - \frac{1}{2}\Delta_2 - \frac{2}{r_1} - \frac{2}{r_2} + \frac{1}{r_{12}}$$

with the nucleus fixed at the origin and with obvious notations. The normalized s orbital of the model is

$$\psi = \frac{1}{r_0} \gamma(r - r_0) Y_{00},$$

which can accommodate two opposite spin electrons. By the axioms of the γ function and property Equation (3), we get the kinetic energy for the two electrons as

$$\mathcal{N} = \frac{1}{\sqrt{2} x_n^n}$$

 $T=\frac{1}{r_0^2},$

which is twice that for a single electron, cf. Equation (5), at the same r_0 . The average of the one-particle potential is

$$V_1 = -\frac{2}{r_1} - \frac{2}{r_2} = -\frac{4}{r_0}.$$

It remains to set up a model to treat the interelectron repulsion $\frac{1}{r_{12}}$. This cannot be done in the usual way if the radial part contains $\gamma(r - r_0)$, since the repulsion integral with the volume elements $dV_i = 4\pi r_i^2$.

$$(11|11) = \frac{1}{16\pi^2 r_0^2} \iint \gamma^2(r_1) \frac{1}{r_{12}} \gamma^2(r_2) dV_1 dV_2$$

is clearly divergent. This again corresponds to classical electrostatics: the repulsion of two charged particles distributed uniformly on the surface of the same sphere is infinite. This excludes a Hartree–Fock-type treatment, in which one electron feels only the averaged field of the other(s). Instead, one has to take into account the angular correlation, ensuring that the two electrons on the surface of the sphere tend to avoid each other by occupying different angular regions.

The most primitive description of the angular correlation is to assume that the two electrons are located always on opposite poles of the sphere (a "north-south model"), their distance being fixed at 2r₀. This leads to the electrostatic repulsion energy

$$I = \frac{1}{2r_0}$$

Combining the above energy terms to form the total energy, one gets

$$E(r_0) = T + V_1 + I = \frac{1}{r_0^2} - \frac{7}{2r_0}$$

for a sphere with radius r₀. Minimizing this energy, the optimal radius becomes

$$r_0 = 4/7 \approx 0.57$$

which is in good agreement with the accepted atomic radius of He (\approx 30 pm \approx 0.56 a. u.). This value of r₀ leads to the optimal energy

The components of this energy, T = 49/16 and V = -49/8, satisfy the virial theorem—this is a consequence of the variational optimization of r_0 . For comparison, the Hartree–Fock ground-state energy of the He atom in a basis set of 14 Gaussian *s*-type orbits is -2.8617 a.u. Sophisticated quantum chemical calculations with full correlation by Hylleraas yield E = -2.9032 a.u., while the experimental result is E = -2.9038.^[43] The energy obtained in the present simple model is slightly below the exact value. This can be rationalized by noting that the "north-south" model is clearly overcorrelated.

6 | SUMMARY AND DISCUSSION

In the model discussed in this paper, a (quasi)classical point-charge particle was characterized by its charge distribution $\delta(r)$. To allow for a QM treatment, a square-integrable and normalized function $\gamma(r)$ was postulated, whose square is associated with $\delta(r)$. Such functions do not exist among distributions, since no consistent associative multiplication can be defined for them. Multiplication of distributions is studied in mathematics in the framework of Colombeau algebra,^[38,39,44] but it appears that no simple solution emerges to define the root of the delta distribution for a straightforward use in QM. We have not yet found any support to construct the γ function satisfying the axioms postulated either here or in ref. [44] where the square root of delta distributions is explicitly mentioned. In the present paper, therefore, the formalism of distributions as

10 of 12 WILEY_CHEMISTRY

functionals has been avoided. Rather, an intuitive treatment is used, based on predefined postulates of $\gamma(x)$ listed in Equation (1) and requiring that basic rules of integral calculus, especially integration by parts, remain valid. It was noted that for integrals containing the product $\gamma \cdot \gamma''$ no restriction emerges, and such integrals were postulated to vanish under axiom Equation (1c). This permits one to interpret the wave function $\gamma(x - x_0)$ as that of a zero-velocity classical particle at point x_0 . However, for integrals containing $\gamma \cdot \gamma'$, one does get a result via integration by parts, and it has led to the fundamental property Equation (3). This property means that terms of the kinetic energy containing first derivatives (such as the radial part of the 3D Laplacian) do contribute to the kinetic energy integral. Second derivative of $x\gamma$ -type expressions also yield terms containing γ' , resulting in a nonzero kinetic energy integral. By these, a consistent calculus necessary for QM treatment of matrix elements containing functions γ emerges, even though no strict proof was found for the existence of γ .

The resulting formalism was applied to construct a bubble model of the H atom. The situation that the electron is distributed on the surface of a sphere of radius r_n is described by the function $\gamma(r - r_n)$. The model yields energies as continuous functions of r_n , but the energy exhibits minima for *s* levels at exact QM energies, reproducing the Balmer formula. When comparing this model to the classical Bohr model, one finds that both models give exact levels, but neither gives exact wave functions. However, the Bohr model does not offer any approximate wave function, while this is provided by $\gamma(r - r_n)$. The Bohr model is artificially quantized, while $E(r_n)$ are continuous functions whose minima correspond to QM situations. Finally, the present model is correctly spherical for *s* states yielding zero angular moments, while the Bohr ground state operates with a planar orbit exhibiting wrong nonzero angular moment.

The fact that for the H atom $\gamma(r - r_n)$ at optimal r_n is not the exact wave function while its energy is exact is quite interesting, since it seemingly contradicts Eckart's theorem.^[45] However, the proof of this theorem is based on the expansion of the approximate wave function based on exact eigenfunctions, and this is impossible to do with function γ which has zero expansion coefficients.

For the harmonic oscillator, description by the γ function provides a rather crude model, the *n*th state describing the particle at points $\pm x_n$ with nonzero kinetic energies. Nevertheless, the spectrum of oscillator levels at optimal x_n , $E_n = n\omega$, is correct, apart from the absence of the zero-point energy. The latter is a genuine QM effect, which is not accounted for by the quasi-classical model studied here.

Both the H atom and the oscillator kinetic and potential energies satisfy the virial theorem, which is a consequence of the variational optimization of r_n and x_n .

Among two-electron systems, the He atom was studied with an approximate account of interelectronic repulsion. The γ function with this overcorrelated model yielded a ground-state energy 0.1587 a.u. below the exact value. Note that this estimation emerges from paper-and-pencil calculation in a couple of lines. The virial theorem is satisfied also for the He atom.

The present bubble model for the H and He atoms is not to be confused with some other interesting models using bubble potentials, that is, a $\delta(r - r_0)$ type potential.^[46,47] In these applications, the introduction of the square root of δ is unnecessary.

Analyzing the examples shown in this paper, some natural questions arise: Is the success of these examples fortuitous? What about the Ansatze used to describe the studied systems, are they unique or arbitrary? Are there any principles for constructing suitable Ansatze for other systems? Can multi-center or many-electron systems be treated by a similar technique?

At the current stage of research, we can provide only partial answers to these questions. As to the systems treated here, the Ansatze are intuitive, but can be justified.

For the harmonic oscillator, two γ functions are set symmetrically at certain distances x_n from the origin, simulating the classical turning points. This is rational because the classical oscillator spends most of its time at the turning points where the velocity is small. The prefactor x^n is a natural choice for the *n*th excited state, separating states of even and odd symmetries.

For H and He atoms, the spherical symmetry is natural to incorporate. The model essentially consists of replacing an exponential-type radial function by $\gamma(r - r_0)$, following the bubble model. The *ns* states for n > 1 differ only from the ground state in applying an r^{n-1} prefactor—this is the simplest possibility to distinguish between states of different *n*. One may note that this idea is based on our previous knowledge about the true QM treatment. One has to mention in this connection that the aim of the present paper was not to develop a theory independent on quantum or classical mechanics but was simply to investigate whether the function $\gamma(x)$ can serve as a "quasi-wave function" in a quasi-classical description.

Further studies are necessary to provide more precise answers to the above questions, to mark the domain of the quasi-classical model based on $\gamma(x)$, to see whether it is applicable to more complicated systems. Work in these lines is in progress.

ACKNOWLEDGMENTS

The author is indebted to Prof. Á. Szabados for discussions and for reading the manuscript. Discussions with Prof. I. Faragó, Dr D. Köhalmi, and Zs. Mihálka are gratefully acknowledged. This work was completed in the ELTE Excellence Program (783-3/2018/FEKUTSRAT) supported by the Hungarian Ministry of Human Capacities, and was partly supported by the grant NKFIH-K115744.

ORCID

Péter R. Surján D https://orcid.org/0000-0002-5714-1846

HEMISTRY-WILEY

REFERENCES

- [1] H. W. Buyck Jr., S. R. Langhoff, Science 1991, 254, 394.
- [2] C. J. Cramer, Essentials of Computational Chemistry, John Wiley & Sons, Chichester 2002, p. 153.
- [3] K. A. Peterson, D. Feller, D. A. Dixon, TCA 2012, 131, 1079.
- [4] T. Furtenbacher, M. Horváth, D. Koller, P. Sólyom, A. Balogh, I. Balogh, A. Császár, J. Phys. Chem. Ref. Data 2019, 48, 023101.
- [5] R. Ts, T. Furtenbacher, J. Tennyson, A. Csaszar, Phys. Chem. Chem. Phys. 2019, 21, 3473.
- [6] T. Helgaker, P. Jørgensen, J. Olsen, Molecular Electronic-Structure Theory, John Wiley & Sons Ltd, New York 2000.
- [7] I. Shavitt, R. J. Bartlett, Many-Body Methods in Chemistry and Physics, Cambridge University Press, Cambridge 2009.
- [8] R. Ahlrichs, S. Elliot, U. Huniar, in Modern Methods and Algorithms of Quantum Chemistry, 2nd ed., Vol. 3 (Ed: J. Grotendorst), John von Neumann Institute for Computing, NIC Series, Jülich 2000, p. 7.
- [9] M. Schütz, G. Hetzer, H.-J. Werner, J. Chem. Phys. 1999, 111, 5691.
- [10] A. Holas, Chem. Phys. Lett. **2001**, 340, 553.
- [11] D. A. Mazziotti, J. Chem. Phys. 2001, 115, 8305.
- [12] H.-J. Werner, F. R. Manby, P. J. Knowles, J. Chem. Phys. 2003, 118, 8149.
- [13] D. Kőhalmi, Á. Szabados, P. R. Surján, Phys. Rev. Lett. 2005, 95, 13002.
- [14] Z. Rolik, L. Szegedy, I. Ladjánszki, B. Ladóczki, M. Kállay, J. Chem. Phys. 2013, 139, 094105.
- [15] M. Bennati, K. Németh, P. R. Surján, M. Mehring, J. Chem. Phys. 1996, 105, 4441.
- [16] M. Kállay, K. Németh, P. R. Surján, J. Phys. Chem. A 1998, 102, 1261.
- [17] P. R. Surján, A. Lázár, M. Kállay, Phys. Rev. B 1998, 58, 3490.
- [18] A. Lázár, P. R. Surján, M. Paulsson, S. Stafström, Int. J. Quantum Chem. 2002, 84, 216.
- [19] P. R. Surján, A. Lázár, Á. Szabados, Phys. Rev. A 2003, 68, 062503.
- [20] A. Szabados, L. P. Biró, P. R. Surján, Phys. Rev. B 2006, 73, 195404.
- [21] P. Szakács, D. Kocsis, P. R. Surján, J. Chem. Phys. 2010, 132, 034309.
- [22] J. B. Keller, SIAM Rev. 1985, 27, 485.
- [23] M. V. Berry, K. E. Mount, Rep. Progr. Phys. 1972, 35, 315.
- [24] M. S. Child, Semiclassical Mechanics with Molecular Applications, 2nd ed., Oxford University Press, Oxford 2014.
- [25] P. V. Grujic, N. S. Simonovic, J. Phys. B: Atom., Mol. Opt. Phys. 1995, 28, 1159.
- [26] C. Harabati, K. G. Kay, J. Chem. Phys. 2007, 127, 084104.
- [27] W. H. Miller, Adv. Chem. Phys. 1974, 25, 69.
- [28] D. J. Tannor, S. Garashchuk, Ann. Rev. Phys. Chem. 2000, 51, 553.
- [29] R. Schinke, J. P. Toennies, J. Chem. Phys. 1975, 62, 4871.
- [30] M. Ceotto, S. Valleau, G. F. Tantardini, A. Aspuru-Guzik, J. Chem. Phys. 2011, 134, 234103.
- [31] G. D. Kolinger, L. F. Canto, R. Donangelo, S. R. Souza, Phys. Rev. C 2018, 98, 044604.
- [32] J. Frenkel, Wave Mechanics-Elementary Theory, Oxford University Press, Oxford 1936.
- [33] G. Wentzel, Zeitshr. Phys. 1926, 38, 518.
- [34] H. A. Kramers, Zeitshr. Phys. 1926, 39, 828.
- [35] L. Schwartz, Théorie des Distributions, Hermann, Paris 1978.
- [36] L. Schwartz, Some Applications of the Theory of Distributions, Wiley, New York 1963, p. 23.
- [37] L. Schwartz, C. R. Acad. Sci. Paris 1954, 239, 847.
- [38] J. F. Colombeau, J. Math. Anal. Appl. 1983, 94, 96.
- [39] J. F. Colombeau, Bull. Am. Math. Soc. 1990, 23, 251.
- [40] C. Runge, Vectoranalysis, Hirzel, Stuttgart 1919.
- [41] W. Lenz, Zeitshr. Phys. 1924, 24, 197.
- [42] U. Ben-Yaakov, J. Math. Phys. 2010, 51, 122902.
- [43] E. A. Hylleraas, Adv. Quant. Chem. 1964, 1, 1.
- [44] G. Hörmann, J. Fourier Anal. Appl. 2018, 24, 1160.
- [45] C. E. Eckart, Phys. Rev. 1930, 36, 878.
- [46] S. M. Blinder, Chem. Phys. Lett. 1979, 64, 485.
- [47] M. Crysos, J. Chem. Phys. 2017, 146, 024106.

How to cite this article: Surján PR. Introducing the γ function in quantum theory. Int J Quantum Chem. 2020;e26221. <u>https://doi.org/10.1002/qua.26221</u>

APPENDIX A

Starting from property Equation (2) of the δ function for n = 2 and using the symbol γ , one writes

$$\int_{-\infty}^{\infty} \left(\gamma(x)^2\right)'' f(x) \, dx = f''(0).$$

Since $(\gamma^2)'' \equiv (2\gamma\gamma')' \equiv 2{\gamma'}^2 + 2\gamma\gamma''$, one gets

$$\int_{-\infty}^{\infty} \gamma'(x)^2 f(x) dx + \int_{-\infty}^{\infty} \gamma(x) \gamma''(x) f(x) dx = \frac{1}{2} f''(0).$$

Rewriting the first integral of the LHS as $\int \gamma' f\gamma' \equiv -\int \gamma(f\gamma')' \equiv -\int \gamma f' \gamma' - \int \gamma f\gamma''$ and substituting it into the previous equation, the term $\int \gamma f\gamma''$ indeed drops out, and one is left with

$$\int_{-\infty}^{\infty} \gamma(x) f'(x) \ \gamma'(x) \ dx = -\frac{1}{2} f''(0),$$

which is the fundamental property found in Equation (3) as applied to *f*'. Some of these points will be addressed in subsequent papers of a series initiated here.