We examine the recently derived quantum-mechanical relation between atomic polarizabilities and equilibrium internuclear distances in van der Waals (vdW) bonded diatomic systems [Phys. Rev. Lett. 121, 183401 (2018)]. For homonuclear dimers, this relation is described by the compact formula \( \alpha_m^d(R_{vdW}) = \Phi R_{vdW}^7 \), where the constant factor in front of the vdW radius was determined empirically. Here, we derive \( \Phi = (4\pi\epsilon_0/a_0^4) \times \alpha^{1/3} \) expressed in terms of the vacuum electric permittivity \( \epsilon_0 \), the Bohr radius \( a_0 \), and the fine-structure constant \( \alpha \). The validity of the obtained formula is confirmed by estimating the value of the fine-structure constant from non-relativistic quantum-mechanical calculations of atomic polarizabilities and equilibrium internuclear vdW distances. The presented derivation allows to interpret the fine-structure constant as the ratio between the polarizability densities of vacuum and matter, whereas the vdW radius becomes a geometrical length scale of atoms endowed by the vacuum field.

Electric polarization, which arises in atoms, molecules, and materials via formation of permanent or transient electric multipoles, is a fundamental property of matter. Similarly, quantum fields possess transient particle/antiparticle pair fluctuations or virtual excitations, which can be characterized by finite polarizability density [4].

Within the classical picture, an atom, as a unit of matter (\( m \)), is described by a hard sphere with its volume \( V_m = 4\pi R_m^3/3 \) filled by a homogeneous electron density surrounding an infinitely-heavy positive point charge. The polarizability of such an atom can be obtained from the dipole moment induced by an external electric field [4, 5],

\[
\alpha_m^c(R_m) = (4\pi\epsilon_0)R_m^3,
\]

which implies that the polarizability density of matter is given by \( \alpha_m^c/V_m = 3\epsilon_0 \). Thus, in a classical picture the polarizability of an atom is intimately connected to its Euclidean volume. However, for real atoms composed of many electrons interacting with a positively-charged nucleus and possessing an inhomogeneous electron density, the atomic radius \( R_m \) is not observable.

A proper quantum-mechanical description implies that a radius of an isolated atom is strictly infinite, since its electron density (although decaying exponentially) is not confined in Euclidean space. Nevertheless, the polarizability is known to increase with an increasing number of electrons for a fixed nuclear charge. Therefore, it is natural to search for an observable atomic size that can be used to predict the polarizability of an atom. In our recent work [5], we accomplished this task by obtaining a compact quantum-mechanical relation between the atomic polarizability and the vdW radius (half of the equilibrium internuclear distance in homonuclear dimers),

\[
\alpha_m^d(R_{vdW}) = \Phi R_{vdW}^7.
\]
tends to zero because the speed of light $c$ tends to infinity [8]. Hence, the FSC enters formulas in a product with the speed of light as $\alpha c$, which is trivially equal to unity in atomic units. To establish the validity of our derivation, we use atomic polarizabilities and equilibrium distances in homonuclear dimers of noble gases computed from non-relativistic quantum-mechanical treatment of valence electrons. Overall, our results suggest an intimate relation between polarizabilities of matter and the underlying vacuum field, yielding insights into the atomic quantum geometry.

We start by expressing the well-known formula for the FSC as a ratio between two polarizability densities

$$\alpha = \frac{c^2/4\pi\epsilon_0}{(\alpha_1 V_1) / \alpha_2 V_2},$$  \hspace{1cm} (4)$$

where $\alpha_{1(2)}$ and $V_{1(2)}$ are the polarizability and volume of two different elements. Given that the FSC measures the interaction between (real or virtual) photons and charged matter particles, we associate one of the polarizability terms to the vacuum field and another one to matter. Let us fix a volume of the field element $V_1 = V_1$ and obtain the associated field polarizability $\alpha_1 = \alpha_1$. Then, determine a volume of the matter element $V_m = V_2$, such that $\alpha_m = \alpha_1$. Under this condition, Eq. (4) can be rewritten as

$$\alpha = \left(\frac{V_m}{V_1}\right)_{\alpha_m=\alpha_1}.$$  \hspace{1cm} (5)$$

The placing of $V_m$ in the numerator and $V_1$ in the denominator is unambiguous and chosen such that the polarizability density of matter becomes larger than that of the vacuum field for a fixed volume by $\alpha^{-1} \approx 137.036$. Equation (5) can also be written in terms of the radii of the field and matter volume elements

$$R_{1}^{3} = \alpha^{-1} R_{m}^{3} \quad \text{and} \quad R_{1} = \alpha^{-1/3} R_{m},$$  \hspace{1cm} (6)$$

under the condition of equal polarizabilities. The physical interpretation of these equations is the following. The polarizability of a vacuum sphere of radius $R_1$ is $\alpha^{-1}$ times smaller than the polarizability of a sphere of matter with the same radius. Our forthcoming analysis confirms that $\alpha$ describes the ratio of polarizability densities of vacuum and matter, enriching the existing spectrum of textbook interpretations of the FSC [8].

As mentioned above, the quantum-mechanical polarizability of matter $\alpha_m^q$ given by Eq. (2) has been derived based on the balance between forces stemming from quantum exchange and correlation interactions [5]. The exchange force arises from the spin-statistics theorem in quantum-field theory [9, 10], which provides further evidence that $\alpha_m^q$ is determined by the interaction between matter and the vacuum field. The classical and quantum expressions for the polarizability of matter, Eqs. (1)–(2), intersect at one and only one critical radius $R_c$ determined by the vacuum field. According to Eq. (6), we define $R_c = \alpha^{-1/3} a_0$, where $a_0$ is the characteristic atomic length scale. Imposing the condition

$$\alpha_m^q(R_c) = \alpha_m^a(R_c),$$  \hspace{1cm} (7)$$

we obtain the polarizability of matter as $(4\pi\epsilon_0/\alpha_0)\alpha^{x/3}$. According to Eqs. (4) and (5), the corresponding field polarizability turns out to be unitary (in atomic units). Finally, using Eq. (7), we identify the proportionality constant in Eq. (2) as

$$\Phi = (4\pi\epsilon_0/\alpha_0) \times \alpha^{x/3}.$$  \hspace{1cm} (8)$$

Thus, the numerical coefficient of $(2.54)^{-7}$ in Eq. (3), which was empirically fixed in Ref. [5] to its average value for the noble gas atoms spanning the range $(2.54 \pm 0.02)^{-7} \approx 0.001388 - 0.001549$, is now specified as $\alpha^{x/3} \approx 0.001415$.

The formula given by Eq. (8) is the central result of our work. Combining Eqs. (2) and (8) yields the final quantum-mechanical expression for the atomic polarizability in terms of three fundamental physical constants and the vdW radius

$$\alpha_m^q = (4\pi\epsilon_0/\alpha_0)^{4/3} R_{vdW}^7.$$  \hspace{1cm} (9)$$

Remarkably, the power $4/3$ in the above equation can also be inferred from the relation between the polarizability and volume of a quantum harmonic oscillator with arbitrary mass and frequency, specified as $\alpha_{QDO} \propto V_{QDO}^{4/3}$ [11, 12]. Indeed, $\alpha^{x/3} a_0$ can be represented as $(\alpha^{-1/3} a_0)^{x/3}$, where $\alpha^{-1/3} a_0$ has units of volume. In our recent work [5], the coefficient $\Phi$ was empirically fitted to polarizabilities and interatomic distances of noble gas dimers. Now we can reconsider this procedure for $\Phi$ derived in terms of the FSC and given by Eq. (8). The statistical analysis in Ref. [5] was done on the prefactor $\Phi^{x/3}$ of the expression for $R_{vdW}$ in terms of $\alpha_m^q$. Hence, here we compare the corresponding $1/\alpha^{x/3} \approx 2.5528$ derived from Eq. (8) to the range $2.54 \pm 0.02$ obtained in Ref. [5] for noble gas atoms. Our analytical derivation falls well within the statistical error bar of the empirical determination with a deviation of just 0.5% from the mean.

A graphical illustration of the accuracy of Eq. (8) is provided by Fig. 1(a), where $R_{vdW}(\alpha_m)$ calculated by Eq. (9) from the accurate values for atomic polarizabilities [11] are shown versus the experimental reference data from Refs. [13, 14]. The atomic polarizabilities and the vdW radii are known for the noble gases with a very high accuracy. This explains the excellent agreement between $R_{vdW}(\alpha_m)$ and $R_{vdW}^{ref}$ in Fig. 1(a) for these atoms. A similar situation is found for organic elements. For other atoms, the reference data is less accurate, because of the increased statistical errors in the tabulated $R_{vdW}^{ref}$ [13]. The worst case corresponds to the transition metals possessing various spin states in the crystal compounds used for the evaluation of their vdW radii from the experimental data. This is the reason for the largest deviations.
between \( R_{\text{vdW}}(\alpha_m) \) and \( R_{\text{vdW}}^{\text{ref}} \) obtained for such chemical elements as Cr (12.88%) and V (12.07%). However, the average relative error for all 72 elements shown in Fig. 1(a) is just 3.07% and it reduces to 0.05% by restricting our consideration to the noble gases only. Thus, the main reason for the observed discrepancies is caused by the statistical error in determination of \( R_{\text{vdW}}^{\text{ref}} \) [13]. In addition, there might be a small influence from higher-order quantum electrodynamic contributions to the atomic polarizabilities, scaling as higher powers of the FSC. Altogether, this analysis validates our derivation of the intimate connection between matter and vacuum polarization processes.

In addition to the discussion of the two vdW radii shown in Fig. 1(a), we compare the radii \( R_m(\alpha_m) \) calculated by means of Eq. (1) to \( R_{\text{vdW}}^{\text{ref}} \) from the experimental reference data collected in Refs. [13, 14]. This comparison is shown in Fig. 1(b), where the dotted line corresponds to the use of \( R_{\text{vdW}}^{\text{ref}}(\alpha_m) \) obtained from Eq. (9) instead of \( R_{\text{vdW}} \), which contain large statistical errors for elements such as transition metals [13]. The value of the two radii, at which Eqs. (1) and (9) possess the same polarizabilities and radii, \( \alpha_m^1 = \alpha_m^2 = (4\pi\epsilon_0)\alpha^{-1/3} a_0^3 \approx 137.036 \text{ a.u. and} R_m = R_{\text{vdW}} = \alpha^{-1/3} a_0 \approx 5.1556 \text{ a.u.}, \) is indicated by the two intersecting lines in Fig. 1(b). Similar to Fig. 1(a), most atoms in the periodic table are close to the dotted line, confirming a simple non-linear relation between \( R_m \) and \( R_{\text{vdW}} \) involving the FSC. As expected, noble gas atoms and organic elements, for which the statistical data for the determination of the vdW radius are abundant, are particularly close to the dotted line. It is worth noting the contrasting behavior of noble gases and alkali metal atoms in Fig. 1(b). While the noble gas series He-Ne-Ar-Kr-Xe-Rn seems to slowly converge towards the “magic” radius of \( R_c = \alpha^{-1/3} a_0 \) from below, the alkali atoms Cs-Rb-K-Na-Li converge to this radius from above. Remarkably, for many elements in the periodic table, \( R_m \) and \( R_{\text{vdW}} \) are relatively close to \( R_c \). This suggests that in the asymptotic case with respect to the atomic number Eqs. (1) and (9) are seamlessly connected. In other words, for macroscopic matter, the quantum-mechanical formula of Eq. (9) transforms to its classical counterpart given by Eq. (1).

It is worth discussing the two radii considered above in more detail. The classical atomic radius \( R_m \) defined by Eq. (1) is also known as the polarizability radius [15, 16]. This radius was introduced based on the fact [17] that for a uniform conducting sphere of radius \( R_m \) the polarizability has the same expression as given by Eq. (1). The polarizability radius has been used in chemical literature together with several other radii [16, 18] aimed to qualitatively represent atomic size and enable comparison between different atoms. The vdW radius was defined by Pauling [19] and Bondi [14] as half of the distance between two (closed-shell) atoms of the same chemical element, at which Pauli exchange repulsion and London dispersion attraction forces exactly balance each other [20]. Based on this definition, in Ref. [5] we derived the scaling law of Eq. (9) and reasonably estimated the constant \( \Phi \), which is finally specified here by Eq. (8).
In the former case, nuclear quantum effects contribute to the vdW radii. Both estimates of the FSC are in good agreement, except for deviations observed for He and Rn.

Our derivation suggests that the vdW radius corresponds to a relation between the length scales in vacuum and matter since balanced forces occur when atoms interact through the vacuum. In other words, one can assume that the vdW radius describes the atomic size endowed by the vacuum field. Therefore, the vdW radius should not strongly depend on the atomic environment. Indeed, the vdW radius for noble gas atoms (except for the lightest He atom) remains practically the same in gas, liquid, and solid states of matter.

An interesting application of Eq. (9) is the possibility to obtain the FSC, which is the dimensionless quantity \( \alpha = e^2/(4\pi\epsilon_0\hbar c) \) arising in relativistic quantum mechanics, by means of non-relativistic quantum-mechanical calculations. One just needs to determine the atomic polarizability \( \alpha_m \) and the equilibrium interatomic distance \( R_{\text{eq}} = 2R_{\text{vdW}} \) in homonuclear vdW-bonded dimers. Both quantities can be computed very accurately from state-of-the-art quantum-chemical methods for closed-shell atoms. The resulting prediction of the FSC is shown in Table I for the six noble gases present in Fig. 1.

| Species | \( \alpha_m \) | \( R_{\text{vdW}}^{\text{calc}} \) | \( R_{\text{vdW}}^{\text{exp}} \) | \( \alpha(R_{\text{vdW}}^{\text{calc}}) \) | \( \alpha(R_{\text{vdW}}^{\text{exp}}) \) |
|---------|----------------|-----------------|-----------------|-----------------|-----------------|
| He      | 1.38           | 2.81            | 2.65            | 0.00561         | 0.00763         |
| Ne      | 2.67           | 2.92            | 2.91            | 0.00753         | 0.00766         |
| Ar      | 11.10          | 3.56            | 3.55            | 0.00774         | 0.00786         |
| Kr      | 16.80          | 3.82            | 3.82            | 0.00730         | 0.00730         |
| Xe      | 27.20          | 4.11            | 4.08            | 0.00713         | 0.00741         |
| Rn      | 32.20          | 4.18            | 4.23            | 0.00741         | 0.00696         |

The atomic polarizabilities and equilibrium internuclear distances have been obtained from high-level calculations based on self-interaction corrected time-dependent density-functional theory for the polarizability and CCSD(T) for binding energy curves. The computed values \( R_{\text{vdW}}^{\text{calc}} \) do not account for nuclear quantum vibrations, particularly important for the He dimer. For this reason, in Table I we also provide comparative estimates of \( \alpha \) obtained using the experimentally determined vdW radii. Both estimates of the FSC are in good agreement, except for deviations observed for He and Rn.

In the former case, nuclear quantum effects contributing to the experimental \( R_{\text{vdW}}^{\text{exp}} \) seem to be the source of the difference. For Rn, the discrepancy is presumably caused by the strong relativistic effects influencing both, the vdW radius and the polarizability. Indeed, with the polarizability of 33.54 a.u. obtained for Rn in Ref. [11] and \( R_{\text{vdW}}^{\text{exp}} = 4.23 \) a.u., the estimated FSC would become 0.007176. Overall, there is good agreement between \( \alpha(R_{\text{vdW}}^{\text{calc}}) \) or \( \alpha(R_{\text{vdW}}^{\text{exp}}) \) from Table I and the well-known reference value \( \alpha \approx 0.007297 \) confirmed by recent measurements. The small uncertainty in the values of the polarizabilities and the vdW radii is not the only reason for the observed discrepancy. It is also likely that the quantum-mechanical formula given by Eq. (9) corresponds to a leading-order approximation. Higher-order terms with respect to the FSC need to be considered for furnishing a more accurate formula.

In summary, we presented the derivation of the prefactor in the quantum-mechanical relation between the atomic polarizability and vdW radius, \( \alpha_m^n = \Phi R_{\text{vdW}}^2 \). This constant factor was shown to be given by the simple expression \( \Phi = (4\pi\epsilon_0/a_0^3) \times a^{4/3} \) in terms of the three fundamental physical constants: the vacuum electric permittivity \( \epsilon_0 \), the Bohr radius \( a_0 \), and the fine-structure constant \( \alpha \). The validity of the derived expression was illustrated by the comparison between the calculated and reference vdW radii. It was shown that the vdW radius describes an atomic size endowed by the vacuum field, which has an intimate connection to the classical atomic radius, \( R_m = (\alpha_m^1/(4\pi\epsilon_0))^{1/3} \), via the polarizability \( \alpha_m \). The quantum and classical formulas for the atomic polarizability intersect at a value \( \alpha_m = \alpha^{-1} \) in atomic units, which corresponds to the unitary polarizability of the vacuum field. Altogether, this indicates that the fine-structure constant describes the ratio between the polarizability densities of the vacuum field and matter.

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[1] J. Rafelski and B. Müller, *The structured vacuum: Thinking about nothing*, (H. Deutsch Publishers, 1985).
[2] P. W. Milonni, *The Quantum Vacuum*, (Academic Press, 1993).
[3] Throughout the paper, all the values of different quantities are given in atomic units with \( h = m = e = 4\pi\epsilon_0 = 1 \). However, for clarity, all physical constants are kept explicitly in the formulas.
[4] P. Atkins and R. Friedman, *Molecular Quantum Mechanics*, (Oxford University Press, 2010).
[5] D. V. Fedorov, M. Sadhukhan, M. Stöhr, and A. Tkatchenko, *Quantum-Mechanical Relation between Atomic Dipole Polarizability and the van der Waals Radius*, Phys. Rev. Lett. 121, 183401 (2018).
[6] A. P. Jones, J. Crain, V. P. Sokhan, T. W. Whitfield, and G. J. Martyna, *Quantum Drude oscillator model of atoms and molecules: Many-body polarization and dispersion interactions for atomistic simulation*, Phys. Rev.
[7] K. T. Tang and J. P. Toennies, An improved simple model for the van der Waals potential based on universal damping functions for the dispersion coefficients, J. Chem. Phys. 80, 3726 (1984).

[8] P. Strange, Relativistic Quantum Mechanics: With Applications in Condensed Matter and Atomic Physics, (Cambridge University Press, 1998).

[9] P. A. M. Dirac, The Principles of Quantum Mechanics, (Clarendon Press, 1930).

[10] W. Pauli, On the Connection between Spin and Statistics, Prog. Theor. Phys. 5, 526 (1950).

[11] V. V. Gobre, Efficient modelling of linear electronic polarization in materials using atomic response functions, PhD thesis, Fritz Haber Institute Berlin (2016).

[12] A. Kleshchonok and A. Tkatchenko, Tailoring van der Waals dispersion interactions with external electric charges, Nature Communications 9, 3017 (2018).

[13] S. S. Batsanov, Van der Waals Radii of Elements, Inorganic Materials 37, 871 (2001).

[14] A. Bondi, van der Waals Volumes and Radii, J. Phys. Chem. 68, 441 (1964).

[15] I. K. Dmitrieva and G. I. Plindov, Dipole Polarizability, Radius and Ionization Potential for Atomic Systems, Phys. Scr. 27, 402 (1983).

[16] R. L. DeKock, J. R. Strikwerda, and E. X. Yu, Atomic size, ionization energy, polarizability, asymptotic behavior, and the Slater-Zener model, Chem. Phys. Lett. 547, 120 (2012).

[17] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, Molecular Theory of Gases and Liquids, (Wiley-Interscience, New York, 1964).

[18] P. Politzer, P. Jin, and J. S. Murray, Atomic polarizability, volume and ionization energy, J. Chem. Phys. 117, 8197 (2002).

[19] L. Pauling, The Nature of the Chemical Bond, (Ithaca: Cornell University, 1960).

[20] F. Nunzi, G. Pannacci, F. Tarantelli, L. Belpassi, D. Cappelletti, S. Falcinelli, and F. Pirani, Leading Interaction Components in the Structure and Reactivity of Noble Gases Compounds, Molecules 25, 2367 (2020).

[21] In the calculations, relativistic effects were included approximately for the core electrons of Xe and Rn. However, the valence electrons predominantly determining the polarizability and the equilibrium distance were calculated using the non-relativistic Schrödinger equation. The contribution of core electrons to the polarizability and the equilibrium distance are negligible for Xe and Rn.

[22] S. S. Batsanov and A. S. Batsanov, Introduction to Structural Chemistry, (Springer, 2012).

[23] T. Gould and T. Bučko, $C_6$ Coefficients and Dipole Polarizabilities for All Atoms and Many Ions in Rows 1–6 of the Periodic Table, J. Chem. Theor. Comput. 12, 3603 (2016).

[24] E. F. Laschuk, M. M. Martins, and S. Evangelisti, Ab Initio Potentials For Weakly Interacting Systems: Homonuclear Rare Gas Dimers, Int. J. Quant. Chem. 95, 303 (2003).

[25] P. Slavíček, R. Kalus, P. Paška, I. Odvárková, P. Hobza, and A. Malijevský, State-of-the-art correlated ab initio potential energy curves for heavy rare gas dimers: $Ar_2$, $Kr_2$, and $Xe_2$, J. Chem. Phys. 119, 2102 (2003).

[26] A. Shee, S. Knechtb, and T. Saue, A theoretical benchmark study of the spectroscopic constants of the very heavy rare gas dimers, Phys. Chem. Chem. Phys. 17, 10978 (2015).

[27] R. S. Davis, Determining the value of the fine-structure constant from a current balance: Getting acquainted with some upcoming changes to the SI, Amer. J. Phys. 85, 364 (2017).

[28] R. H. Parker, C. Yu, W. Zhong, B. Estey, and H. Müller, Measurement of the fine-structure constant as a test of the Standard Model, Science 360, 191 (2018).

[29] P. Cladé, F. Nez, F. Biraben, and S. Guellati-Khelifa, State of the art in the determination of the fine-structure constant and the ratio $h/m_u$, Compt. Rend. Phys. 20, 77 (2019).