Comment on “Long-Range Repulsion Between Spatially Confined van der Waals Dimers”

Recently, Sadhukhan and Tkatchenko (ST) derived formulas for interaction energies of Coulomb-coupled two one- (1D), two- (2D), and anisotropic three-dimensional (3D) quantum harmonic oscillators (QHOs) [1], serving as models for interacting spatially confined molecules. As a leading term of a $1/R^n$ expansion, where R is the distance between the QHO centers, they find a repulsive $O(1/R^5)$ term for all cases, whereas for two isotropic 3D oscillators the leading (attractive) term is $O(1/R^6)$, as expected for systems interacting via dispersion forces only. In the 1D case, ST's term reads

$$\epsilon_1 = 2\frac{\alpha_2 \hbar\omega}{R^5}, \tag{1}$$

with ω denoting the circular frequency of the fully separated QHOs, $\alpha_2 = \frac{3}{4}(q^2\hbar/m^2\omega^3)$ the quadrupole-quadrupole polarizability of an uncoupled QHO, m the mass, and q the magnitude of the charge of the oscillating particles, balanced by opposite charges at the spatially fixed centers. From Eq. (1), ST conclude, “The appearance of quadrupole polarizability α_2 (…) in the leading repulsive term (…) indicates that ϵ_1 corresponds to the mean-field energy of an instantaneous quadrupole in the field generated by fluctuations in another electronic fragment.” Moreover, ST reject that the interaction is due to electrostatic effects stating, “We remark that even when such confinement entails tiny modification of the electron density (having no apparent effect on the electrostatics), it can visibly affect the interactions stemming from density fluctuations...” ST draw similar conclusions for the case of interacting 2D and anisotropic 3D oscillators.

Here, we point out that the physical picture of repulsive charge fluctuations implied by the statements of ST is incorrect: it is rather the interaction between the *static* quadrupole moments of 1D, 2D, and anisotropic 3D QHOs (resulting from breaking of the spherical symmetry [2]) that generates the repulsive $O(1/R^5)$ contribution. In an eigenstate of an overall electrically neutral 1D QHO, instantaneous dipole moments of equal magnitude but opposing directions occur with identical probabilities. Charge and dipole expectation values thus vanish but not the quadrupole moment—notice that antiparallel dipoles of equal magnitude represent a quadrupole. The linear (i.e., extremely prolate [3]) average charge distribution of a 1D QHO thus creates an inhomogeneous static electric field acting on a second QHOs quadrupole to yield (Eq. (3.2.8) of Ref. [4] for $\theta_A = \theta_B = \phi = 0$)

$$\epsilon_1 = \frac{6\Theta_\parallel^A \Theta_\parallel^B}{R^5}, \tag{2}$$

where $\Theta_\parallel^A$, $\Theta_\parallel^B$ are the parallel components of the diagonal traceless Cartesian quadrupole moments tensor for the oscillators A and B, respectively. Since for the ground state of identical 1D oscillators $\Theta_\parallel^A = \Theta_\parallel^B = -q\hbar/2m\omega$, Eq. (2) becomes numerically identical to Eq. (1) but provides the correct physical picture which also leads to a different experimental signature through considering differing spatially confined atoms: their interaction energy must contain products of properties of *both* [4]. If Eq. (2) were to describe interactions between fluctuations in both systems, as suggested by ST, it would have to include a product of *two* polarizabilities. Also, static quadrupole moments of spatially confined atoms, in principle, can be measured.

For the 2D case, ST consider planar axial-symmetric oscillators. Their (extremely oblate [3]) charge distributions generate perpendicular quadrupole components $\Theta_\perp = q\hbar/2m\omega$. The leading term of the interaction energy between two coplanar oscillators thus reads [4]

$$\epsilon_1 = \frac{9\Theta_\perp^A \Theta_\perp^B}{4R^5} = \frac{9q^2\hbar^2}{16m^2\omega^2}\frac{1}{R^5}, \tag{3}$$

numerically identical to Eq. (21) of Ref. [1], but again very different in its physical content. The same conclusions for the 1D and 2D models obtained from perturbation theory were given in Ref. [2].

Since the static quadrupole moment vanishes for spherically symmetric systems [3], there is no $O(1/R^5)$ term for interacting *isotropic* 3D oscillators. In their anisotropic 3D case, ST add a half-oscillator in the perpendicular direction to the 2D oscillator, now $\Theta_\perp = q\hbar/m\omega$, and using the lhs of Eq. (3), the final energy becomes identical to Eq. (79) of the Supplemental Material of Ref. [1]. However, this model also possesses a nonzero dipole moment, resulting in an additional repulsive interaction energy of $(4q^2\hbar/m\omega\pi)(1/R^3)$. Lateral repulsion of physisorbed molecules with permanent and surface-induced dipole moments has already been included in early models of gaseous adsorption [5] and improves modeling of the adsorption isotherm [6].

R. P. acknowledges support from the Polish National Science Centre Grant No. 2015/17/B/ST4/03727. G. J. acknowledges support from the Deutsche Forschungsgemeinschaft (DFG) within the priority programme SPP 1807 “Control of London Dispersion Interactions in Molecular Chemistry” (Grant No. JA954/4-1). We are grateful to ST for pointing out Ref. [2].

Rafał Podeszwa
Institute of Chemistry, University of Silesia
Szkolna 9, 40-006 Katowice, Poland
Georg Jansen
Theoretical Organic Chemistry, Department of Chemistry
University Duisburg-Essen
Universitätsstraße 5, D-45117 Essen, Germany

Received 9 August 2017; published 20 June 2018
DOI: 10.1103/PhysRevLett.120.258901

[*]rafal.podeszwa@us.edu.pl
[†]georg.jansen@uni-due.de

[1] M. Sadhukhan and A. Tkatchenko, Long-Range Repulsion between Spatially Confined van der Waals Dimers, Phys. Rev. Lett. **118**, 210402 (2017).

[2] A. C. Ipsen and K. Splittorff, The van der Waals interaction in one, two, and three dimensions, Am. J. Phys. **83**, 150 (2015).

[3] I. G. Kaplan, *Intermolecular Interactions* (Wiley, Chichester, 2006), p. 31.

[4] A. J. Stone, *The Theory of Intermolecular Forces*, 2nd ed. (Oxford University Press, Oxford, 2013).

[5] A. Magnus, Theorie der Gasadsorption, Z. Phys. Chem. **142A**, 401 (1929).

[6] D. D. Do and H. D. Do, Effects of quadrupole moments of graphite surface on adsorption of simple gases on graphitized thermal carbon black, Colloids Surf., A **300**, 50 (2007).