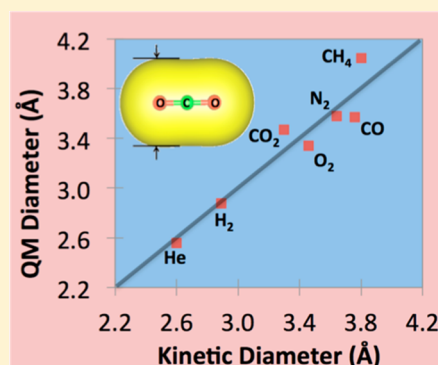


Quantum Mechanical Basis for Kinetic Diameters of Small Gaseous Molecules

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ABSTRACT: Kinetic diameters are often invoked in discussing gas adsorption and permeation in porous and polymeric materials. However, how these empirical kinetic diameters relate to the size and shape of the molecules as manifested by their “electron cloud” is unclear. In this paper, we obtain the quantum mechanical (QM) diameters of several common gaseous molecules by determining the cross-sectional sizes of their iso-electronic density surfaces at a predetermined small value. We show that the QM diameters are in good agreement with the kinetic diameters. For example, the trends for important gas pairs such as O₂ versus N₂ and CO₂ versus N₂ are consistent between the QM diameters and the most often quoted kinetic diameters. Hence, our work now provides a quantum mechanical basis for the empirical kinetic diameters and will be useful for designing separation media for small gaseous molecules according to their sizes.



I. INTRODUCTION

Beyond conventional crystalline porous materials (namely, zeolites),¹ novel materials have been increasingly utilized for gas separations in recent years, such as polymeric membranes,^{2–6} metal–organic frameworks,^{7–11} covalent organic frameworks,^{12–14} graphene membranes,^{15–23} and amorphous porous materials.^{24–28} Likewise, ionic liquids have been utilized in gas separations as well.^{29–36} As such, an increased emphasis has been placed on understanding the gas separation process in these materials in terms of gas adsorption and permeation. Central to these discussions is the correlation between the size of a gas and the behavior of adsorption and diffusion that the gas exhibits inside the separation medium. To date, gas sizes used have been determined either empirically, such as the kinetic diameter, or via models of molecular interactions, such as the Lennard-Jones diameter.^{1,2} In particular, a common set of kinetic diameters has been most cited in the literature.^{1,2}

The widely quoted kinetic diameters for common gases are from a book on zeolites written by Breck and published in 1974.¹ These diameters in Breck's book were in fact from the earlier work by Hirschfelder, Curtiss, and Bird (HCB).³⁷ HCB derived the kinetic diameters for small gas molecules (such as He, H₂, and N₂) by using the experimental second virial coefficients of gases at different temperatures and assuming that the intermolecular interaction follows the Lennard-Jones potential, $\Phi(r) = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6]$, where σ is the intermolecular distance at which $\Phi(r) = 0$. Breck called this σ the kinetic diameter.^{1,2}

Several shortcomings have been noted for the Breck kinetic diameters.² First, the kinetic diameters obtained from fitting second virial coefficient data to the Lennard-Jones potential often differ from the numbers obtained by fitting gas viscosity data to the Lennard-Jones potential.² Second, a number of

differing Lennard-Jones parameters frequently offer equivalent fits of an experimental data set, thus complicating the identification of unique molecular diameters that are applicable under a variety of experimental conditions.²

Despite those shortcomings, the Breck kinetic diameters for small gases (i.e., σ values as obtained by fitting experimental second virial coefficient data to the Lennard-Jones potentials) are widely quoted in gas adsorption and separation studies, suggesting that those numbers do offer a very useful guideline in considering gas selectivity by size sieving.^{1,2} The question we would like to address here is: Do those numbers have a quantum mechanical basis? In other words, how do those empirical kinetic diameters relate to the molecular shapes of the gases as defined by the “electron clouds” or electron densities that can be derived from ab initio quantum mechanical (QM) calculations? To address this question, herein we use the results from ab initio calculations to derive QM diameters for He, H₂, O₂, N₂, CO, CO₂, and CH₄, and compare them with the Breck kinetic diameters.

II. METHODS

TURBOMOLE V6.5 electronic structure package³⁸ was used for density functional theory calculations at the PBE0 level of theory.³⁹ A triple- ζ valence basis with polarization, specifically, the def2-TZVP orbital and auxiliary basis set, was employed. Once optimized molecular geometries were obtained, iso-electronic density surfaces or contours were generated. A number of density contours at different values (0.001, 0.0015, and 0.002 au or e/a₀³ where a₀ is the Bohr radius) were tested

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in order to find cross-sectional QM diameters closest in comparison to the experimentally determined kinetic diameters for all the gases considered. The cross-sectional diameters were determined from the contour plots that define the molecular shapes in three dimensions. For the small molecules we consider here, this QM diameter could be straightforwardly determined from the shapes of the molecules as indicated by the two arrows in each shape (Figure 1) and explained in Results and Discussion.

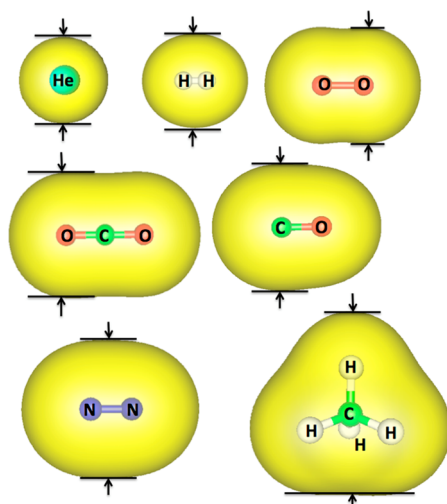


Figure 1. Iso-electronic density surfaces of the He, H₂, O₂, CO₂, CO, N₂, and CH₄ gas molecules plotted at contour level 0.0015 au.

III. RESULTS AND DISCUSSION

The most straightforward way to define a shape of a molecule is to compute the electron density of the molecule, pick a small value, and plot the three-dimensional (3D) iso-value surface. This 3D iso-electron density surface represents the electron cloud or bounded space that the molecule occupies. Now imagine that this rather rigid 3D shape flows through a tube of a diameter d . The smallest d that the 3D molecular shape can still diffuse through will be the cross-sectional diameter of the molecule. We call this diameter the quantum mechanical (QM) diameter of the molecule, as the electron density is derived from the QM calculation consistently for all the gases. Of course, for a specific molecule, its QM diameter will depend on the small value we use to define the boundary of the electron cloud. Table 1 lists the QM diameters of seven common gases

Table 1. Quantum Mechanical (QM) Diameters of Common Gases as Determined by the Iso-Electron Density Surfaces of Different Values (0.001, 0.0015, and 0.002 a.u.); Breck Kinetic Diameters Are Included for Comparison

gas	QM diameter (Å)			kinetic diameter (Å) ¹
	0.001	0.0015	0.002	
He	2.699	2.557	2.422	2.60
H ₂	3.106	2.877	2.760	2.89
O ₂	3.444	3.340	3.184	3.46
N ₂	3.622	3.578	3.360	3.64
CO	3.593	3.570	3.376	3.76
CO ₂	3.536	3.469	3.297	3.30
CH ₄	4.142	4.046	3.815	3.80

measured at iso-electron density values of 0.001, 0.0015, and 0.002 au (or e/a_0^3), in comparison with the Breck kinetic diameters. At first glance, it can be seen that the QM diameters obtained at all isovalues or contour levels represent a good correlation with the Breck kinetic diameters. The contour level at 0.0015 au yields the QM diameters that are closest in value to the Breck kinetic diameter when considering the seven molecules all together. This conclusion is clearer if we plot the QM diameters against the Breck kinetic diameters (Figure 2).

Figure 2a plots the QM diameters versus the kinetic diameters at iso-electron density of 0.001 au. The blue line in the figure is representative of the ideal correlation between the QM diameters and the kinetic diameters. Good agreement between the QM diameters and kinetic diameters is observed for N₂, O₂, and He. The QM diameters of H₂, CO₂, and CH₄ obtained at 0.001 au are larger than their corresponding kinetic diameters, while the trend is reversed for CO. As a whole, the QM diameters measured at the iso-electron density value of 0.001 au displayed a correlation of 0.852 with the Breck kinetic diameters in terms of R^2 (Table 2).

Figure 2b plots the QM diameters against the kinetic diameters obtained at iso-electron density value of 0.0015 au. When the proximity of the points relative to the correlation line and the R^2 values in Table 2 are compared, it becomes evident that the best correlation between the QM and kinetic diameters are obtained at contour level 0.0015 au. Best agreement is observed for He, H₂, and N₂; the QM diameters obtained for CO₂ and CH₄ are bigger than their corresponding kinetic diameters, while the QM diameters of O₂ and CO are smaller than their corresponding kinetic diameters.

Figure 2c plots the QM diameters against the kinetic diameters of the gases obtained at iso-electron density value of 0.002 au. As the value increases, the molecular volume shrinks and all dimensions decrease. Hence, it is expected that the majority of the QM cross-sectional diameters derived at contour level 0.002 au are now smaller than their corresponding kinetic diameters. The QM diameters of CO₂ and CH₄ at contour level 0.002 au show the best agreement with their corresponding kinetic diameters.

It is clear from Figure 2c that 0.002 au defines an upper limit for the iso-electron density value; higher than this value, the molecular shape and its associated dimensions obtained are too small when considering the sizes of these small molecules for adsorption and diffusion in porous materials. The 0.0015 au contour level seems to be a good choice that yields molecular dimensions most consistent with the commonly employed Breck kinetic diameters. Given that the ground-state electronic density is well-described by a hybrid functional such as PBE0 used here, we expect that this value of 0.0015 au should be quite universal in giving a good estimate of molecular dimensions.

The QM diameters obtained for O₂ and N₂ at iso-electronic density level of 0.0015 au are consistent with their respective Breck kinetic diameters. As noted in Table 1, both the QM and kinetic diameters of N₂ are approximately 0.2 Å greater than those of O₂. Moreover, this is consistent with the relative positions of N and O in the periodic table: because of the more positively charged nucleus of O, its electrons feel a stronger pull from the nucleus; hence, O has a smaller diameter. As anticipated, this translates into greater permeability and selectivity of O₂ in some carbon molecular sieves^{40,41} and composite hollow fiber membranes.^{42–44}

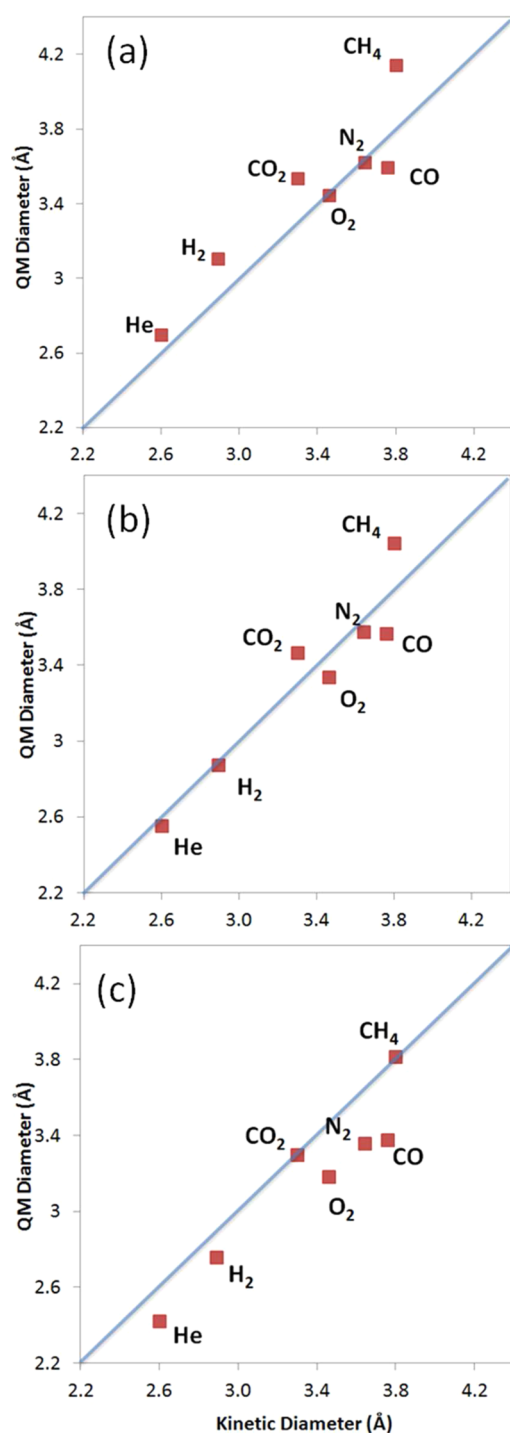


Figure 2. Quantum mechanical (QM) diameters versus the Breck kinetic diameters¹ at different iso-electron density values: (a) 0.001; (b) 0.0015; (c) 0.002 au.

Table 2. Least-Squares Fit of Quantum Mechanical (QM) Diameters of Common Gases at Different Iso-Electron Density Values (a.u.) against Their Respective Breck Kinetic Diameters¹

isovalue	0.001	0.0015	0.002
R^2	0.852	0.900	0.896
slope	0.914	1.025	0.945

The relative trend of the QM diameters obtained for CO_2 and N_2 at iso-electronic density level 0.0015 au is also consistent with that from the Breck kinetic diameters. Moreover, this is supported by recent experimental and computational studies in which CO_2 was shown to be more permeable than N_2 in nanoporous graphene^{18,21,45} and in composite hollow fiber membranes.⁴⁶ The QM diameter of N_2 is basically the same as that of CO (within 0.01 Å) at iso-electronic density level 0.0015 au, while the Breck kinetic diameter of N_2 is 0.12 Å smaller than that of CO . It is reasonable that N_2 and CO have a similar QM diameter because the two molecules have the same number of bonds and bonding electrons.

CO_2 and O_2 QM diameters (obtained at iso-electron density value of 0.0015 au) display a different trend from that of the Breck kinetic diameters. The QM diameter obtained for O_2 is 0.13 Å smaller than that of CO_2 , but the Breck kinetic diameter of O_2 is 0.16 Å larger than that of CO_2 . One can understand the QM trend by looking at Figure 1: because O is more electronegative than C, the O atom in CO_2 is negatively charged while the O atom in O_2 is neutral; since the diameter is essentially determined by the electron cloud on the O atom, the negatively charged O atom on CO_2 yields a greater QM diameter. Here we note that Breck¹ did not follow HCB³⁷ to define the kinetic diameter for CO_2 as for other small gases. According to HCB, CO_2 should have a kinetic diameter of 4.07 Å.³⁷ Breck thought this value too big when compared with the kinetic diameter of N_2 at 3.64 Å, based on the experimental observation that the KA zeolite adsorbs CO_2 but not N_2 at similar conditions.¹ Breck therefore suggested 3.3 Å as the kinetic diameter for CO_2 based on the Pauling width of the CO_2 molecule.¹ Using the QM diameter at the iso-electron density value of 0.0015 au for a comparison (3.47 Å), the Breck kinetic diameter for CO_2 might slightly underestimate the size of CO_2 .

It is of course oversimplified to use a single parameter to characterize the size of a nonspherical molecule, either a QM diameter or a kinetic diameter. The electron cloud may be distorted by the electric field of the adsorbent. This should be the case especially for zeolites with extra-framework cations such as KA. Figure 3 displays the electrostatic potential of CO_2 (mapped against its 0.005 au iso-electron density contour), which shows a partial positive charge on carbon and partial

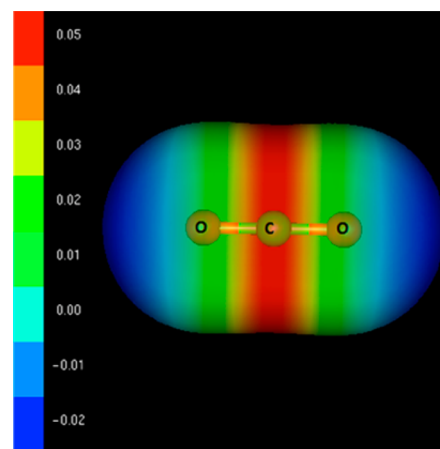


Figure 3. Electrostatic potential representations of CO_2 mapped against iso-electron density value of 0.005 au.

negative charges on both oxygen atoms. One can imagine that when such a molecule is adsorbed into a zeolite cage of inhomogeneous electric field, the electron cloud will reshape and the QM diameter may not truly reflect the molecular size.

For separation media of less polarizing nature, such as polymers and porous carbons, we believe that the QM diameters offer a good description of the relative size trend of the small gas molecules. The advantages of the QM diameters over the Breck kinetic diameters are that they offer a consistent description based on the ab initio calculations, while the Breck kinetic diameters not only depend on the experimental second virial coefficients but also have to make a special case for CO₂.

IV. SUMMARY AND CONCLUSIONS

The empirical Breck kinetic diameters have been widely utilized in explaining gas sorption and transport in porous and polymeric materials. Here we have determined the quantum mechanical (QM) diameters for those gases and compared them with the Breck kinetic diameters. A generally good agreement has been found, despite some discrepancies that have been discussed in detail. This work provides a quantum mechanical foundation for the empirical Breck kinetic diameters for small gaseous molecules such as He, H₂, O₂, N₂, CO, CO₂, and CH₄ and should be useful for discussing the size-selectivity of gases in separation media.

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Notes

The authors declare no competing financial interest.

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