

A simple and surprisingly accurate approach to the chemical bond obtained from dimensional scaling

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We present a new dimensional scaling transformation of the Schrödinger equation for the two electron bond. This yields, for the first time, a good description of the two electron bond via D-scaling. There also emerges, in the large-D limit, an intuitively appealing semiclassical picture, akin to a molecular model proposed by Niels Bohr in 1913. In this limit, the electrons are confined to specific orbits in the scaled space, yet the uncertainty principle is maintained because the scaling leaves invariant the position-momentum commutator. A first-order perturbation correction, proportional to $1/D$, substantially improves the agreement with the exact ground state potential energy curve. The present treatment is very simple mathematically, yet provides a strikingly accurate description of the potential energy curves for the lowest singlet, triplet and excited states of H_2 . We find the modified D-scaling method also gives good results for other molecules. It can be combined advantageously with Hartree-Fock and other conventional methods.

Quantum chemistry has achieved excellent agreement between theory and experiment, even for large molecules, by using computational power to overcome the difficulty of treating electron-electron interactions [1, 2, 3, 4]. Here we present a new version of an unconventional method to treat electronic structure [5, 6, 7, 8]. This emulates an approach developed in quantum chromodynamics [9], by generalizing the Schrödinger equation to D dimensions and rescaling coordinates [7].

Early work found the tutorial D-scaling procedure of Witten [9] can be dramatically improved; the ground state energy of He was obtained accurate to 5 significant figures by interpolation between the $D = 1$ and $D \rightarrow \infty$ limits [5], and to 9 figures by a perturbation expansion in $1/D$ [10]. However, the scaling procedure which worked well for atoms [5, 6] did not prove successful for two-center problems [7, 8]; e.g., for H_2 that procedure did not yield a bound ground state, (see our Fig. 3).

In our present approach, the large-D limit makes contact with the Bohr model of the H_2 molecule [11]. In this way we obtain, for the first time, a link between pre- and post-quantum mechanical descriptions of the chemical bond (Bohr-Sommerfeld vs Heisenberg-Schrödinger). Marked improvement is achieved by including the leading correction term in $1/D$ and a rudimentary adjustment of the D-scaling. Fig. 1 shows potential energy curves for H_2 obtained with our simple approach. Dots comprise a synthesis of experimental data and computations employing many terms in variational wavefunctions [12]. Our simple method gives surprisingly accurate results and holds promise for numerous applications.

We first outline our method as applied to H_2 and then indicate how it differs from what preceded [7, 8]. Fig. 2 displays electron distances in the H_2 molecule. All distances are expressed in terms of the Bohr length $a_0 = \hbar^2/me^2$, where m is the electron mass, and energies are in the Hartree unit e^2/a_0 . We start with $\hat{H}\Psi = E\Psi$,

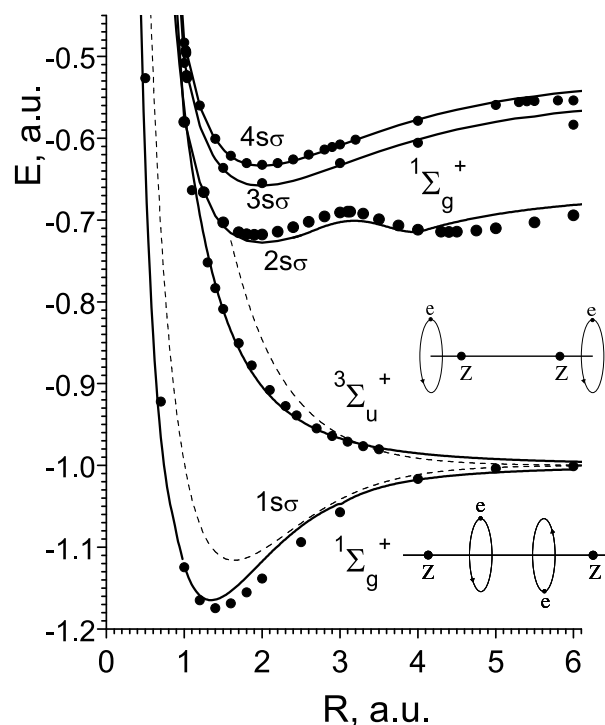


FIG. 1: Potential energy (solid curves) of the ground and a few excited states of H_2 obtained from the Bohr model with D-scaling analysis. Dots are the “exact” energies [12]. The inserted figures on the right hand side depict the two nuclei of charge Z and Bohr’s “planetary” orbits for the electrons in the $1\Sigma_g^+$ and $3\Sigma_u^+$ states (see also Fig. 4). Dashed curves are from Heitler-London treatment [13].

for H_2 :

$$\hat{H} = -\frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 + V(\rho_1, \rho_2, z_1, z_2, \phi).$$

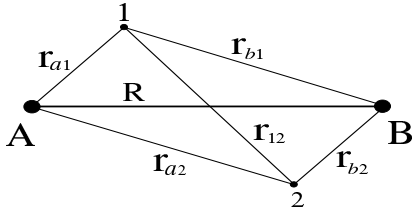


FIG. 2: Electronic distances in H_2 molecule. The nuclei A and B are fixed a distance R apart.

The Coulomb potential energy V is given by

$$V = -\frac{Z}{r_{a1}} - \frac{Z}{r_{b1}} - \frac{Z}{r_{a2}} - \frac{Z}{r_{b2}} + \frac{1}{r_{12}} + \frac{Z^2}{R}, \quad (1)$$

in terms of distances defined in Fig. 2. In cylindrical coordinates

$$r_{ai} = \sqrt{\rho_i^2 + \left(z_i - \frac{R}{2}\right)^2}, \quad r_{bi} = \sqrt{\rho_i^2 + \left(z_i + \frac{R}{2}\right)^2},$$

$$r_{12} = \sqrt{(z_1 - z_2)^2 + \rho_1^2 + \rho_2^2 - 2\rho_1\rho_2 \cos \phi},$$

where R is the internuclear spacing and ϕ the dihedral angle between the planes containing the electrons ($i = 1, 2$) and the internuclear axis.

We proceed by endowing each vector with D cartesian coordinates [7]. The potential energy V is retained [14] in the three dimension form of Eq. (1) whereas the Laplacians in the kinetic energy take the form

$$\nabla^2 = \frac{1}{\rho^{D-2}} \frac{\partial}{\partial \rho} \left(\rho^{D-2} \frac{\partial}{\partial \rho} \right) + \frac{1}{\rho^2} \frac{\partial^2}{\partial \varphi^2} + \frac{\partial^2}{\partial z^2}. \quad (2)$$

We then scale coordinates by f^2 and energy by $1/f^2$, with $f = (D-1)/2$, and transform the wavefunction Ψ by

$$\Psi = (\rho_1 \rho_2)^{-(D-2)/2} \Phi. \quad (3)$$

This recasts the Schrödinger equation as

$$(K_1 + K_2 + U + V)\Phi = E\Phi, \quad (4)$$

where

$$K_i = -\frac{2}{(D-1)^2} \left\{ \frac{\partial^2}{\partial \rho_i^2} + \frac{\partial^2}{\partial z_i^2} + \frac{1}{\rho_i^2} \frac{\partial^2}{\partial \phi^2} \right\},$$

$i = 1, 2$ and

$$U = \frac{(D-2)(D-4)}{2(D-1)^2} \left(\frac{1}{\rho_1^2} + \frac{1}{\rho_2^2} \right). \quad (5)$$

In the limit $D \rightarrow \infty$ the derivative terms in K_i are quenched. The corresponding energy E_∞ for any given

internuclear distance R is then obtained simply as the extremum of the effective potential, $U + V$, given by

$$E = \frac{1}{2} \left(\frac{1}{\rho_1^2} + \frac{1}{\rho_2^2} \right) + V(\rho_1, \rho_2, z_1, z_2, \phi, R). \quad (6)$$

This is exactly the energy function that applies to the Bohr model of the molecule [11].

The usual D-scaling procedure [7, 8] involves setting up the full Laplacian in D -dimension and transforming the wavefunction by incorporating the square root of the Jacobian via $\Psi \rightarrow J^{-1/2}\Phi$, where $J = (\rho_1 \rho_2)^{D-2} (\sin \phi)^{D-3}$. Then, on scaling the coordinates by f^2 and the energy by $1/f^2$, the Schrödinger equation in the limit $D \rightarrow \infty$ yields

$$E = \frac{1}{2} \left(\frac{1}{\rho_1^2} + \frac{1}{\rho_2^2} \right) \frac{1}{\sin^2 \phi} + V(\rho_1, \rho_2, z_1, z_2, \phi, R), \quad (7)$$

which differs from Eq. (6) by the factor $1/\sin^2 \phi$.

Our procedure, designed to reduce to the Bohr model at the large- D limit, instead incorporates only the radial portion of the Jacobian in transforming the wavefunction via Eq. (3). This has important consequences. Fig. 3 displays the $D \rightarrow \infty$ potential energy curve of Eq. (7) (dashed curve, “full- J ”); which exhibits no binding. However, our “Bohr model” limit obtained from Eq. (6) yields a good zero-order approximation for the ground state (curve 2 in Fig. 3). It is surprisingly accurate at both large and small internuclear distances R . Also, the model predicts the ground state is bound with an equilibrium separation $R_e = 8/(9 - \sqrt{3}) \approx 1.10$ and gives the binding energy as $E_B = 3(2 - \sqrt{3})/8$ a.u. ≈ 0.100 a.u. $= 2.73$ eV. The Heitler-London calculation (shown in Fig. 1, dashed curve), obtained from a two-term variational function, gives $R_e = 1.51$ and $E_B = 3.14$ eV [13], whereas the “exact” results are $R_e = 1.401$ and $E_B = 4.745$ eV [1].

For the triplet ${}^3\Sigma_u^+$ state, as seen in Fig. 1, the Bohr model energy function of Eq. (6) gives a remarkably close agreement with the “exact” potential curve and is in fact much better than the Heitler-London result (which, e.g., is 30% high at $R = 2$).

In essence, D-scaling procedures resemble gauge transformations. Many varieties of scaling are feasible, subject only to the constraint that as $D \rightarrow 3$ the scaled Schrödinger equation reduces to the correct form. The basic aim is to devise a scaling that removes the major, generic D-dependence, enabling the easily evaluated $D \rightarrow \infty$ limit to approximate the $D = 3$ energy. With the “full- J ” scaling previously used [8], when D is increased the $(\sin \phi)^{D-3}$ factor in the Jacobian forces ϕ towards 90° , while minimization of electron-electron repulsion requires $\phi \rightarrow 180^\circ$. The effect is to overweight electron repulsion; this is the chief source of the failure to obtain chemical bonding in previous work. Our new procedure avoids such overweighting by retaining the $D = 3$ form for the ϕ -part of both the Jacobian and the Laplacian of Eq. (2). Thereby ϕ remains a fully quantum variable

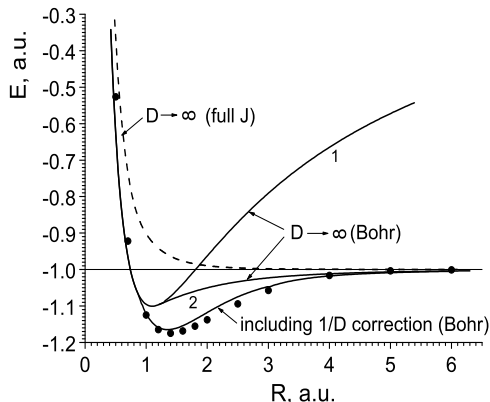


FIG. 3: Energy $E(R)$ of H_2 molecule in the limit $D \rightarrow \infty$ calculated from Eq. (7) (dashed curve) and from the Bohr model of Eq. (6) (solid curves). Curve 1 corresponds to a symmetric configuration obtained by Bohr [11] and pictured in Fig. 4 (top). Curve 2 describes an asymmetric solution (not found by Bohr), see Fig. 4 (bottom). Lower solid curve is the improved ground state $E(R)$ after including $1/D$ correction.

as $D \rightarrow \infty$, rather than being converted to a semiclassical parameter along with the ρ and z coordinates. This much improves description of the electron repulsion and hence the chemical bonding.

The scaling procedure enables, in the large- D limit, calculations to be carried out in the scaled space that are entirely classical. The extremum equations $\partial E/\partial z = 0$ and $\partial E/\partial \rho = 0$ are equivalent to Newton's second law applied to the motion of each electron. Respectively, they specify that the net Coulomb force on the electron along the z -axis vanishes and that the projection of the Coulomb force perpendicular to the molecular axis balances the centrifugal force. Although the electrons are thereby confined to specific orbits in the scaled space, the uncertainty principle is nonetheless satisfied. This is so because the conjugate momenta are scaled inversely to the coordinates, leaving the position-momentum commutator invariant. The continuous transition between the scaled space and the unscaled space in effect relates classical trajectories at large- D to corresponding quantum distributions at $D=3$. This aspect becomes particularly evident when treating electronic tunneling [7].

Fig. 4 displays the “exact” electron charge density along the molecular axis in the ground state of H_2 for internuclear spacing $R = 0.8$ and 1.4 a.u. Circles show electron orbits in Bohr's model. The orbit positions for any R actually coincide with the maxima in the charge density. This provides a link between the wave mechanical and Bohr ($D \rightarrow \infty$ limit) treatments of the H_2 bond.

The ground state $E(R)$ can be substantially improved by use of a perturbation expansion in powers of $1/D$, developed by expanding the effective potential of Eq. (6)

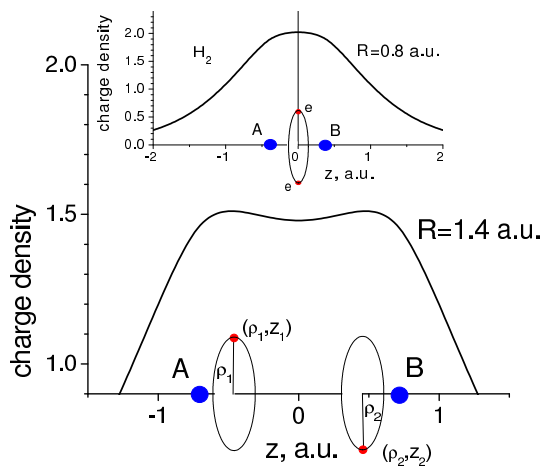


FIG. 4: Distribution of the electron charge density in the H_2 molecule along the molecular axis z . The nuclei are fixed a distance R apart. Circles are electron orbits in Bohr's model.

in powers of the displacement from the minimum [7]; for He this has yielded highly accurate results [10]. Terms quadratic in the displacement describe harmonic oscillations about the minimum and give a $1/D$ correction to the energy. A symmetry breaking point occurs at $R_c = 1.2$, beyond which the electron orbits move apart (c.f. Fig. 4). Such symmetry breaking is a typical feature exhibited as Z or R is varied at large- D [7, 15]. The $1/D$ correction works well at points substantially below or above R_c . Results for those regions thus can be combined. This involves transforming the axial coordinates to $z_1 \pm z_2$, in order to separate the double-well structure that occurs in $z_1 - z_2$. With the other coordinates fixed at their values at the minimum of $U + V$, a one-dimensional Schrödinger equation is solved to take into account the double-well mode. This contribution to the $1/D$ correction corresponds to electron resonance or exchange. The result gives good agreement with the “exact” $E(R)$ over the full range of R (lower solid line in Fig. 3). The $1/D$ correction predicts the equilibrium separation to be $R_e = 1.38$ with binding energy $E_B = 4.50$ eV.

The Bohr and D -scaling techniques taken together hold promise for numerous applications. In particular, these provide a new approach to treating excited states. For example, in our analysis the energy of $1s2s$ state of the He atom is obtained as an extremum of the energy function $E = n_1^2/2r_1^2 + n_2^2/2r_2^2 + V(\mathbf{r}_1, \mathbf{r}_2)$, where $n_1 = 1$ and $n_2 = 2$; $\mathbf{r}_1, \mathbf{r}_2$ are electron radius vectors and V is the Coulomb potential energy. This yields the value of -2.159 a.u. which differs by 0.7% from the “exact” $1s2s$ energy of -2.144 a.u. For other excited states of He as well as more complex atoms the combination of the Bohr and D -scaling approaches also provides accurate results; we will discuss this elsewhere.

Fig. 1 demonstrates application of our technique to a few excited states of the H_2 molecule. In treating $1^1\Sigma_g^+$ excited states, we incorporate D -scaling analysis at large R and the exact $E(R)$ of the H_2^+ molecular ion which

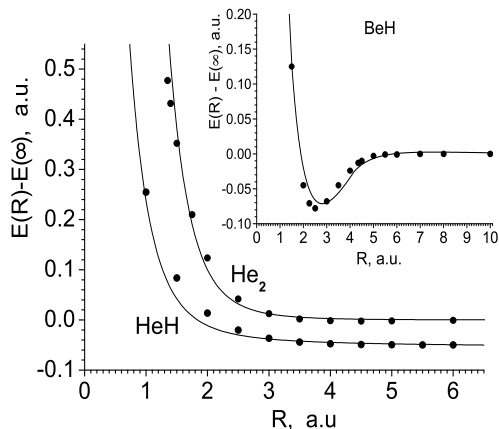


FIG. 5: Ground state $E(R)$ of HeH, He₂ and BeH molecules calculated within the Bohr model (solid curves). The HeH curve is shifted down for clarity.

provides a good description in the remaining region. We have also found the present $D \rightarrow \infty$ limit (Bohr model) gives good results for other molecules; examples so far treated include HeH, He₂, and BeH, pictured in Fig. 5, and LiH, Li₂, Be₂, and the triatomics BeH₂ and H₃ [16].

Another useful strategy is to combine the present approach with conventional electronic structure methods. At $D = 3$, evaluation of the correlation energy, E_{corr} (error in the Hartree-Fock approximation) is the major difficulty. However, at $D \rightarrow \infty$, E_{corr} can be evaluated exactly. Results for He and other atoms [7] show that E_{corr} for $D \rightarrow \infty$ is smaller than but comparable to that for $D = 3$. For the ground state of H₂ we find an accurate energy curve $E(R)$ can be obtained by adding the $D \rightarrow \infty$ correlation energy to the $E(R)$ given by the Heitler-London effective charge method. The result is practically identical to the curve obtained from the $1/D$ correction (Figs. 1 and 3).

Our modified D-scaling procedure reincarnates the Bohr model. This requires only elementary concepts and (laptop) computations yet provides a rather good description of electron-electron interaction and chemical bonding. The procedure is readily applicable to many-electron molecules, both ground and excited states. These results encourage efforts to further improve D-scaling and to augment conventional variational methods for electronic structure to incorporate the exact correlation energy attainable at the large-D limit.

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