Generalizations of Bohr model and the method of dimensional scaling for diatomic and polyatomic molecules

Contents

I. INTRODUCTION

A semiclassical approach which is known as $1/D$, large-D expansion, or sometimes as "dimensional scaling" has a long history. The method is based on the fact that the large-D limit where D is the number of Cartesian dimensions appears to give the spectrum exactly. The method was used more than thirty years ago in quantum field theory and statistical mechanics where it was known as the large-N expansion. Use of the method in non-relativistic quantum mechanics was originally left largely unnoticed, because it was ap-

plied mostly to systems of one effective degree of freedom where direct integration of Schrödinger equation gives more accurate results with less efforts.

For the case of a harmonic oscillator potential, the large-D limit gives the energy exactly. It is no longer valid for the case of one particle confined in Coulomb potential. Nevertheless, a simple scaling of the energy by a factor of $(D-1)^2$ eliminates all $1/D$ corrections in the Coulomb energy, and forces the large-D limit to coincide with the exact energy. Using similar scaling for helium atom gives highly accurate energy even in low orders of the expansion. Using large-D expansion for a hydrogen molecule or its positive ion is compounded by instability of the system in the large-D limit against dissociation. Earlier approaches addressed the problem of large-D instability either by an appropriate scaling of the internuclear separation or using complex extension[1]. Recently, a new generalization of the method of dimensional scaling produced surprisingly accurate results for a hydrogen molecule and for simplest molecules[2, 3]. This approach is based on keeping the angular dependence in the kinetic energy in three-dimensional form while using a D-dimensional version of the radial dependence. It makes the large-D limit resemble the physical three-dimensional problem to a larger extent than it was so for the traditional approach. As a result, the large-D limit of hydrogen molecule becomes stable.

Here, we firstly introduce the large-D approach for the simplest example of quantum mechanical isotropic oscillator in D dimensions. Then, we explain necessity of re-scaling of large-D limit in the case of a hydrogen atom. For helium atom, we show improvement of accuracy of the re-scaled version. We analyze reasons of instability of molecules and weakly bound Coulomb

systems like H^- in large-D limit and compare earlier approaches addressing this problem. We give an outline of the new method emphasizing similarities between the large-D limit and an old Bohr theory of electrons classically moving on circular orbits. We present results for the ground and first excited state of a hydrogen molecule. Finally, we suggest further refinements and generalizations of the model that allow to treat higher excited states of H_2 as well as many-electron molecules.

II. D-DIMENSIONAL ISOTROPIC HARMONIC OSCILLATOR

Hamiltonian of D-dimensional isotropic harmonic oscillator is

$$H = \frac{1}{2m}\boldsymbol{p}^2 + \frac{\omega^2}{2}\boldsymbol{r}^2, \tag{1}$$

where ω is frequency. The radius-vector $\boldsymbol{r}$ has D Cartesian components,

$$\boldsymbol{r} = (r_1, r_2, \ldots, r_D)\,, \tag{2}$$

and the momentum $\boldsymbol{p}$ in coordinate representation equals to gradient times $\left(\frac{\hbar}{i}\right)$,

$$\boldsymbol{p} = \frac{\hbar}{i}\left(\frac{\partial}{\partial r_1}, \frac{\partial}{\partial r_2}, \ldots, \frac{\partial}{\partial r_D}\right). \tag{3}$$

For the ground state, the wave function is radially symmetric, and Schrödinger equation has the form

$$H\psi(r) = E\psi(r), \tag{4}$$

where E is the energy, and the wave function $\psi(r)$ depends only on one variable which is radius $r = \left(\boldsymbol{r}^2\right)^{1/2}$. Derivatives of the wave function are as

follows,

$$\begin{aligned}\frac{\partial\psi(r)}{\partial r_i} &= \frac{r_i}{r}\psi'(r),\\ \frac{\partial^2\psi(r)}{\partial r_i^2} &= \frac{1}{r}\psi'(r)+\frac{r_i^2}{r^2}\left(\psi''(r)-\frac{1}{r}\psi'(r)\right).\end{aligned} \tag{5}$$

Using equation (5), the kinetic energy is expressed as

$$\frac{\boldsymbol{p}^2}{2m}\psi(r) = -\frac{\hbar^2}{2m}\sum_{i=1}^{D}\frac{\partial^2\psi(r)}{\partial r_i^2} = -\frac{\hbar^2}{2m}\left[\psi''(r)+\frac{D-1}{r}\psi'(r)\right]. \tag{6}$$

Thus, the Schrödinger equation is reduced to a differential equation in one variable r,

$$-\frac{1}{2}\left[\psi''(r)+\frac{D-1}{r}\psi'(r)\right]+\frac{\omega^2}{2}r^2\psi(r) = E\psi(r), \tag{7}$$

where we use for simplicity units where $\hbar = m = 1$.

It is convenient to introduce a function $P(r) = r^{\frac{D-1}{2}}\psi(r)$ and to rewrite equation (7) in an equivalent form without linear derivatives,

$$-\frac{1}{2}\frac{d^2P}{dr^2}+\left[\frac{(D-1)(D-3)}{8r^2}+\frac{\omega^2}{2}r^2-E\right]P(r) = 0. \tag{8}$$

The function $P(r)$ is called *radial* wave function because the corresponding density $|P(r)|^2$ equals to the probability to find the particle at one particular point located at distance r from the origin, e. g. $|\psi(r)|^2$, times the area of D-dimensional sphere $\sim r^{D-1}$, which totally gives the probability to find the particle somewhere on the sphere of radius r.

In order to find the large-D limit of equation (8), it is convenient to make a scaling transformation $r \to \widetilde{r} = D^{1/2}r$ and to rewrite equation (8) in the form

$$-\frac{1}{2D^2}\frac{d^2\widetilde{P}}{d\widetilde{r}^2}+\left[\frac{1}{8\widetilde{r}^2}\left(1-\frac{1}{D}\right)\left(1-\frac{3}{D}\right)+\frac{\omega^2}{2}\widetilde{r}^2-\widetilde{E}\right]\widetilde{P}(\widetilde{r}) = 0, \tag{9}$$

where $\widetilde{P}(\widetilde{r}) = P(D^{-1/2}\widetilde{r})$ and $\widetilde{E} = D^{-1}E$. In equation (9), the quantity of $1/D$ in the kinetic energy plays the same role as Plank's constant. For large D, the ground state of quantum mechanical problem approaches the lowest classical state in the potential $V_{\rm eff} = \frac{1}{8\widetilde{r}^2} + \frac{\omega^2}{2}\widetilde{r}^2$ that is the particle resting at the minimum of this potential at $\widetilde{r} = \widetilde{r}_0 = (2\omega)^{-1}$ with energy $\widetilde{E} = \widetilde{E}_0 = \omega/2$.

We could obtain the large-D behavior rigorously, without appealing to analogy between $1/D$ and Plank's constant and the physical argument of classical limit. Let us expand the potential in equation (9) in powers of $1/D$,

$$U(\widetilde{r}) \equiv \frac{1}{8\widetilde{r}^2}\left(1-\frac{1}{D}\right)\left(1-\frac{3}{D}\right)+\frac{\omega^2}{2}\widetilde{r}^2 = U_0(\widetilde{r})+U_1(\widetilde{r})/D+U_2(\widetilde{r})/D^2, \quad (10)$$

where $U_0(\widetilde{r}) = \frac{1}{8\widetilde{r}^2}+\frac{\omega^2}{2}\widetilde{r}^2$, $U_1(\widetilde{r}) = -\frac{1}{2\widetilde{r}^2}$, $U_2(\widetilde{r}) = \frac{3}{8\widetilde{r}^2}$. We shall sometimes refer to U_0 as the *effective potential* $V_{\rm eff}$. The effective potential has a minimum at $\widetilde{r} = \widetilde{r}_0 = (2\omega)^{-1/2}$. We expand U_0, U_1, and U_2 in Taylor series around the point $\widetilde{r}_0$,

$$U_0(\widetilde{r}) = \frac{\omega}{2} + 2\omega^2(\widetilde{r}-\widetilde{r}_0)^2 + 2^{3/2}\omega^{5/2}(\widetilde{r}-\widetilde{r}_0)^3 + 5\omega^3(\widetilde{r}-\widetilde{r}_0)^4 + O(\widetilde{r}-\widetilde{r}_0)^5, \quad (11)$$

$$U_1(\widetilde{r}) = -\omega + 2^{3/2}\omega^{3/2}(\widetilde{r}-\widetilde{r}_0) - 6\omega^2(\widetilde{r}-\widetilde{r}_0)^2 + O(\widetilde{r}-\widetilde{r}_0)^3, \quad (12)$$

$$U_2(\widetilde{r}) = \frac{3}{4}\omega + O(\widetilde{r}-\widetilde{r}_0). \quad (13)$$

Then, we change the variable $\widetilde{r} \to x = D^{1/2}(\widetilde{r}-\widetilde{r}_0)$ and rewrite equation (9) in the form of a harmonic oscillator plus anharmonic corrections,

$$-\frac{1}{2}\frac{d^2y}{dx^2} + [v(x)-\epsilon]\,y(x) = 0, \quad (14)$$

where $y(x) = \widetilde{P}(\widetilde{r}_0 + D^{-1/2}x)$ is a scaled wavefunction and $\epsilon = D\widetilde{E}$ is scaled

energy. The potential in equation (14) is

$$v(x) = DU\left(\widetilde{r}_0 + D^{-1/2}x\right) \tag{15}$$

$$= \frac{\omega}{2}D + 2\omega^2x^2 + 2^{3/2}\omega^{5/2}x^3D^{-1/2} + 5\omega^3x^4D^{-1} - \omega \tag{16}$$

$$+ 2^{3/2}\omega^{3/2}xD^{-1/2} - 6\omega^2x^2D^{-1} + \frac{3}{4}\omega D^{-1} + O(D^{-3/2}). \tag{17}$$

In the limit of $D \to \infty$, the potential tends to

$$v(x) \to v_0(x) = \frac{\omega}{2}D - \omega + \frac{\Omega^2}{2}x^2, \tag{18}$$

where $\Omega = 2\omega$. This is a potential of a harmonic oscillator with a frequency Ω plus a constant. The ground-state energy of the harmonic oscillator is $\frac{1}{2}\Omega$. Adding the constant term $\frac{\omega}{2}D - \omega$, we obtain

$$\epsilon \to \epsilon_0 = \frac{1}{2}\Omega + \frac{\omega}{2}D - \omega = \frac{\omega}{2}D. \tag{19}$$

equation (19) could be generalized for any excited S-state by replacing the oscillator's ground state energy $\frac{1}{2}\Omega$ by the excited state $(n_r + \frac{1}{2})\Omega$, where $n_r = 0, 1, 2, \ldots$. It gives the result $\left(2n_r + \frac{d}{2}\right)\omega$, which is exact energy of radially-symmetric states of D-dimensional oscillator, see Eq. (29) of the paper [10]. Thus, large-D limit coincides with the exact answer both for the ground and for any excited S-state.

Calculating the anharmonic correction is more cumbersome. It could be done using standard formulas of Rayleigh - Schrödinger perturbation theory, by considering the potential correction $2^{3/2}\omega^{5/2}x^3D^{-1/2} + 5\omega^3x^4D^{-1} + 2^{3/2}\omega^{3/2}xD^{-1/2} - 6\omega^2x^2D^{-1} + \frac{3}{4}\omega D^{-1}$ as perturbation. The resulting correction to ϵ is of order D^{-1} with the proportionality coefficient equal to zero. We finally obtain

$$\epsilon \sim \frac{\omega}{2}D + o(D^{-1}). \tag{20}$$

Using relations between scaled and unscaled energies, $\widetilde{E} = D^{-1}\epsilon$ and $E = D\widetilde{E}$, we could see that $E = \epsilon$. So, equation (20) holds also for the unscaled energy E. It is of course consistent with the exact answer for D-dimensional oscillator which is $\frac{\omega}{2} \times D$.

It is important that the large-D limit $E = D\widetilde{E}_0$ is exactly the same as quantum result $\frac{\omega}{2} \times D$. It ensures that at least for some class of potentials resembling harmonic oscillator, the theory will give very accurate predictions in the large-D limit.

Using the large-D limit for a harmonic oscillator is illustrated on Fig 1.

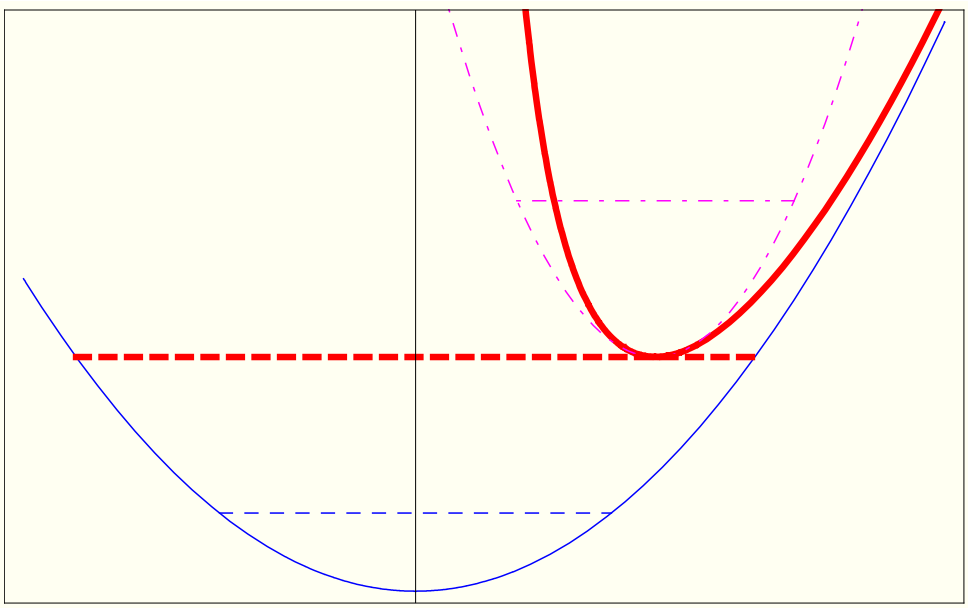

FIG. 1. Calculating the ground-state energy of three-dimensional harmonic oscillator using large-D approach. Thin solid curve is the potential of one-dimensional harmonic oscillator $v(x) = \frac{\omega^2}{2}x^2$, and thin dashed line is its ground-state energy $\frac{1}{2}\omega$. Thick solid curve is the effective potential for three-dimensional oscillator $u_0(r) = \frac{\omega^2}{2}r^2 + \frac{D^2}{8r^2}$. Thick dashed line is the energy of three-dimensional oscillator $\frac{3}{2}\omega$ coinciding with the minimum of the effective potential that gives the leading-order $1/D$ behavior. Dot-dashed curve is the harmonic approximation for the effective potential that has the ground-state energy $\frac{5}{2}\omega$ (dot-dashed line). This extra energy is canceled by an extra energy shift caused by the potential u_1, and it does not affect the large-D limit.

III. D-DIMENSIONAL HYDROGEN ATOM

Hamiltonian of D-dimensional hydrogen atom is

$$H = \frac{1}{2}\boldsymbol{p}^2 - \frac{1}{|\boldsymbol{r}|}, \tag{21}$$

where $\boldsymbol{r}$ and $\boldsymbol{p}$ are D-dimensional vectors, see equations (2) and (3), and the functional form of the Coulomb potential is assumed to be the same for any dimensionality.

In order to obtain the large-D behavior quantitatively, we change the variable $\widetilde{r} \to x = D^{1/2}(\widetilde{r} - \widetilde{r}_0)$ where $\widetilde{r} = D^{-1}r$, $\widetilde{r}_0 = 2$ and rewrite equation (9) in the form of a harmonic oscillator plus anharmonic corrections ...

...

In the large-D limit the scaled energy $\widetilde{E} = D^2 E$ approaches the minimum of the potential $V_{\text{eff}} = \frac{1}{8\widetilde{r}^2} - \frac{1}{\widetilde{r}}$ which is -2, and the unscaled energy approaches $-\frac{2}{D^2}$. The exact quantum energy is given by D-dimensional generalization of Rydberg formula, $E = \frac{4}{2(D-1)^2}$. At $D = 3$, the large-D approximation comprises only 44% of the exact quantum energy. The result could be improved by taking into account quantum harmonic oscillations around the minimum and anharmonic corrections. It leads to so-called $1/D$ expansion,

$$\widetilde{E} = -2 - 2/D - 2/D^2 - \dots. \tag{22}$$

Although the series is slowly convergent, a more direct way is to take into account a double pole of the energy as a function of D at $D = 1$ and to use a different scaling transformation $\widetilde{r} = (D-1)^{-1}r$, $\widetilde{E} = (D-1)^2 E$. This approach allows to calculate the energy exactly just as $D \to \infty$ limit [Herschbach].

Calculating large-D limit for a hydrogen atom is illustrated on Fig 2.

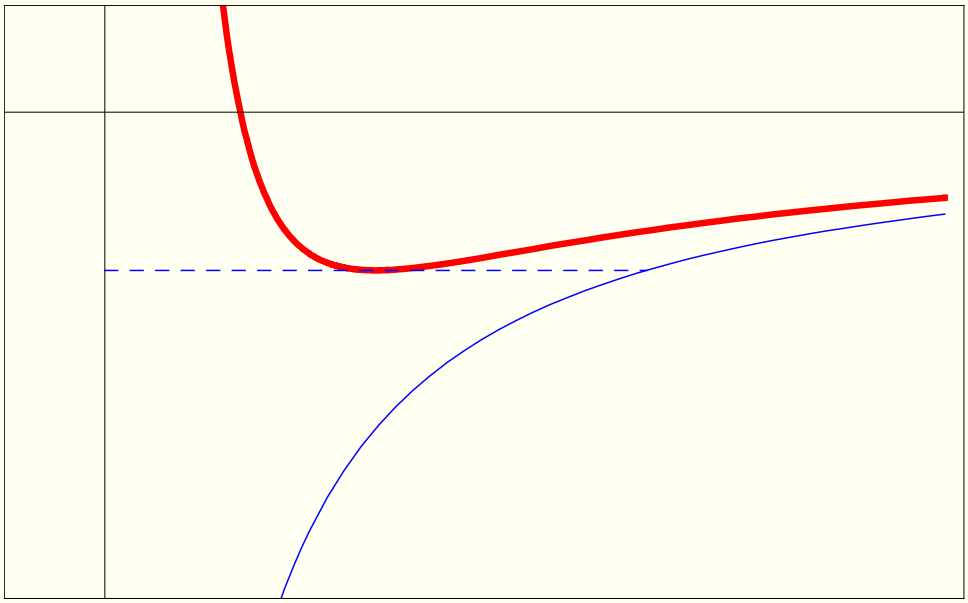

FIG. 2. Calculating the ground-state energy of a hydrogen atom using large-D approach. Thin solid curve is Coulomb potential $v(r) = -1/r$. Thick solid curve is the effective potential (including centrifugal term) $u_0(r) = -1/r + \frac{(D-1)^2}{8r^2}$. Note that we use a scaling $(D-1)^2$ instead of D^2. Dashed line is the ground state energy of a hydrogen atom $-\frac{1}{2}$ coinciding with the minimum of the effective potential that gives the leading-order $1/D$ behavior.

IV. D-DIMENSIONAL HELIUM ATOM

We could expect that $(D-1)$ version of coordinate scaling will give exact results in the large-D limit for other Coulombic systems like several noninteracting electrons in Coulomb field, and not exact, but possibly accurate results for the case of interacting electrons. Here, we test the method for the simplest example of a helium atom. Hamiltonian of D-dimensional helium is

$$H = \frac{1}{2}\boldsymbol{p}_1^2 + ... - \frac{1}{|\boldsymbol{r}_1|}... \tag{23}$$

...

The $1/D$-expansion in its traditional version is

$$\widetilde{E} = \left(\frac{D}{2}\right)^2 E = -2.7378 - 6.0576\left(\frac{2}{D}\right) - 8.8622\left(\frac{2}{D}\right)^2 + \ldots, \qquad (24)$$

while the re-scaled version is

$$\widetilde{E} = \left(\frac{D-1}{2}\right)^2 E = -2.7378 - 0.5821\left(\frac{2}{D}\right) + 0.5152\left(\frac{2}{D}\right)^2 + \ldots, \qquad (25)$$

While the unscaled version gives only 42% of energy in the large-D limit ($\frac{4}{9} \times 2.7378$ vs. 2.9037 exact), the scaled version gives 94% of energy (2.7378 vs. 2.9037 exact). It shows that the singularity at $D = 1$ significantly contributes to the functional behavior (as a function of $1/D$). After factoring-out this singularity, the $1/D$ corrections become small, and the large-D limit becomes an accurate approximation.

V. LARGE-D LIMIT FOR H_2^+. EARLIER APPROACHES

A hydrogen positive ion is the simplest diatomic molecule. Here, we consider a D-dimensional generalization of H_2^+.

Let us consider Cartesian coordinate system $(r_1, r_2, \ldots r_D)$ in D-dimensional space. We will refer to the $D-1$ dimensional vector $(r_1, r_2, \ldots, r_{D-1})$ as $\boldsymbol{\rho}$ and to the last coordinate r_D as z. We introduce a hypothetical D-dimensional potential

$$V(\boldsymbol{r}) = -\frac{1}{\sqrt{\boldsymbol{\rho}^2 + (z - R/2)^2}} - \frac{1}{\sqrt{\boldsymbol{\rho}^2 + (z + R/2)^2}} + \frac{1}{R}, \qquad (26)$$

where the parameter R is interpreted as *separation distance*. The solution of D-dimensional Schrödinger equation with the potential $V(\boldsymbol{r})$, $\Psi(\boldsymbol{r})$, is considered as D-dimensional generalization of the wave function of H_2^+, and

corresponding eigenvalue E is considered as D-dimensional generalization of the energy.

Here, we restrict ourselves to a manifold of wavefunctions depending only on two variables, $\rho = |\boldsymbol{\rho}|$ and z, i.e. $\Psi = \psi(\rho, z)$. In three-dimensional case, those are wavefunctions with zero z-component of the angular momentum. Using the identity

$$\sum_{i=1}^{D} \frac{\partial^2 \Psi}{\partial r_i^2} = \frac{\partial^2 \psi}{\partial \rho^2} + \frac{D-2}{\rho}\frac{\partial \psi}{\partial \rho} + \frac{\partial^2 \psi}{\partial z^2}, \tag{27}$$

we rewrite Schrödinger equation in the form

$$-\frac{1}{2}\left[\frac{\partial^2 \psi}{\partial \rho^2} + \frac{D-2}{\rho}\frac{\partial \psi}{\partial \rho} + \frac{\partial^2 \psi}{\partial z^2}\right] + V(\rho, z)\,\psi = E\psi, \tag{28}$$

where we use "atomic units" with $\hbar = m = 1$. After introducing a function $P(\rho, z) = \rho^{\frac{D-2}{2}}\psi(\rho, z)$, equation (28) takes the form

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial \rho^2} - \frac{1}{2}\frac{\partial^2}{\partial z^2} + \frac{(D-2)(D-4)}{8\rho^2} + V(\rho, z)\right] P(\rho, z) = EP(\rho, z). \tag{29}$$

After a scaling transformation $\widetilde{\rho} = (D-1)^{-2}\rho$, $\widetilde{z} = (D-1)^{-2}z$, $\widetilde{E} = (D-1)^2 E$, we rewrite equation (29) in the form

$$\left[-\frac{1}{2(D-1)^2}\frac{\partial^2}{\partial \widetilde{\rho}^2} - \frac{1}{2(D-1)^2}\frac{\partial^2}{\partial \widetilde{z}^2} + \frac{(D-2)(D-4)}{8(D-1)^2\widetilde{\rho}^2} + \widetilde{V}(\widetilde{\rho}, \widetilde{z})\right] \widetilde{P}(\widetilde{\rho}, \widetilde{z}) = \widetilde{E}\widetilde{P}(\widetilde{\rho}, \widetilde{z}), \tag{30}$$

where $\widetilde{P}(\widetilde{\rho}, \widetilde{z}) = P((D-1)^2\widetilde{\rho}, (D-1)^2\widetilde{z})$ and

$$\widetilde{V}(\widetilde{\rho}, \widetilde{z}) = -\frac{1}{\sqrt{\widetilde{\rho}^2 + (\widetilde{z} - \widetilde{R}/2)^2}} - \frac{1}{\sqrt{\widetilde{\rho}^2 + (\widetilde{z} + \widetilde{R}/2)^2}} + \frac{1}{\widetilde{R}}, \tag{31}$$

with $\widetilde{R} = (D-1)^{-2}R$.

Now, let us consider a limiting case of $D \to \infty$, assuming that $\widetilde{R} = R_0/4 = \text{const}$ far all D which means that $R = R_0$ for $D = 3$ and that R

grows $\sim (D-1)^2$ with increase of D. Since $1/(D-1)$ plays the role of Plank's constant in equation (31), the wave function concentrates around the minimum of the effective potential

$$V_{\text{eff}}(\rho, z) = -\frac{1}{\sqrt{\rho^2 + (z - R_0/8)^2}} - \frac{1}{\sqrt{\rho^2 + (z + R_0/8)^2}} + \frac{4}{R_0}, \qquad (32)$$

that corresponds to a classical particle resting at the minimum. For simplicity, tildes were dropped from equation (32).

The function given by equation (32) has a single global minimum if $R_0 \leq R_\star \approx 1.299$ at $z = 0$ and a pair of symmetric minima at $z = \pm z_0 \neq 0$ if $R_0 > R_\star$. Results of minimization for different separation distances are shown on Fig. 3 taken from the paper [7] where this problem was considered in the most systematic way. In the limit of large D the energy curve on Fig. 3 has no minimum. It means that the molecule is unstable against dissociation. In addition, the equilibrium distance $R \approx 2$ is larger than $R_\star$. Here, the effective potential has two minima. The method cannot distinguish symmetric and antisymmetric states because they are given by the same large-D limit of the particle resting in one of the minima.

The problem of dissociation instability in the large D limit is very general for atomic and molecular systems [8]. The instability is associated with the antisymmetric stretch mode of vibrations. Many papers were devoted to understanding of this pathology, but this impediment had not been circumvented for long time. There were at least two successful approaches addressing this problem. In [1], the author used $1/D$-expansion around the saddle point ($z = 0$), $E(D) = E^\star + E_1 D^{-1}$. Normally, the coefficient E_1 is complex-valued because of purely imaginary frequency of the stretch mode.

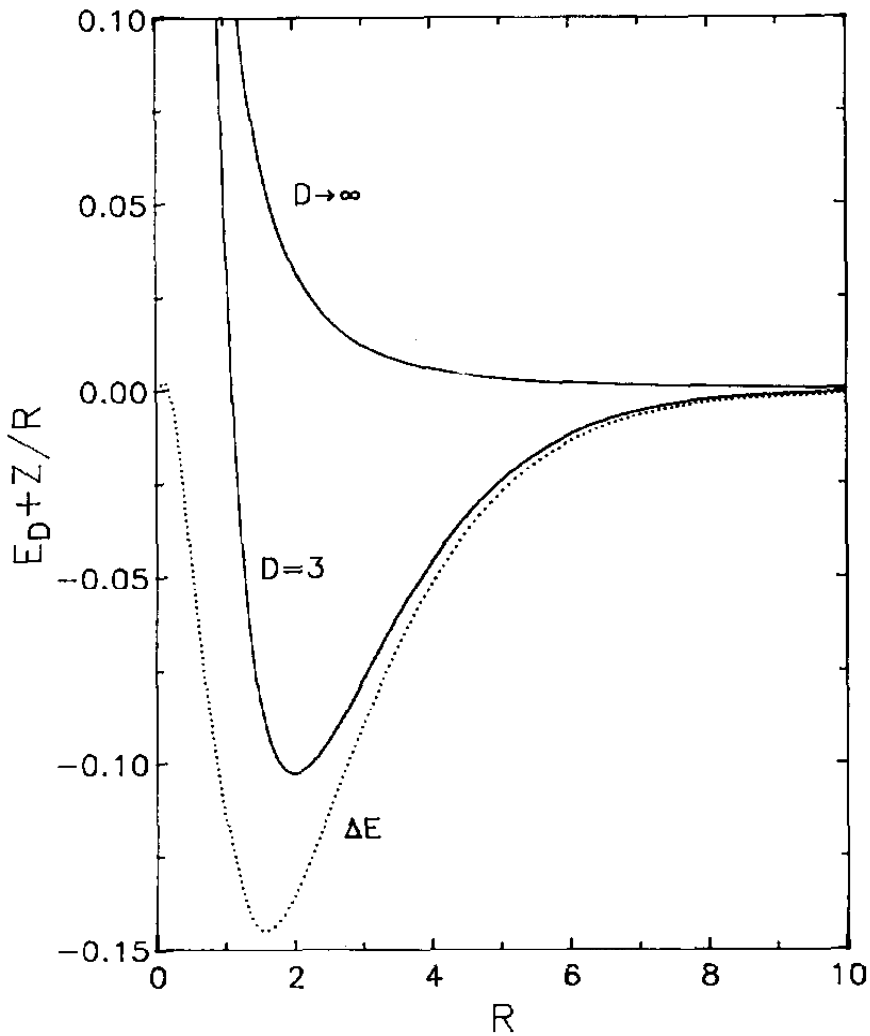

Fig. 10. Variation with R of H_2^+ total energy for $D\to\infty$ obtained by adding scaled nuclear repulsion, Z/R, to the electronic energy (from fig. 4). Also shown is the corresponding curve for $D=3$ (from ref. [6]). Dotted curve is the difference between the $D\to\infty$ and $D=3$ curves.

FIG. 3. Ground state energy for H_2^+ for $D = 3$ and in the large-D limit. The figure is taken from the paper [7]

The author used method of complex rotation in order to make this correction real. He found for H_2^+ $E(3) = -0.6046$ vs. exact energy -0.6026, i.e. he achieved an accuracy of 0.3%. In the paper [5], the author used dimensional interpolation between $D = 1$ and $D = \infty$ limits. While the curve at $D = \infty$

is purely repulsive, the curve at $D = 1$ is purely attractive. The interpolated curve $\frac{1}{3}E(1) + \frac{2}{3}E(\infty)$ is repulsive at small R, attractive at large R, and it possesses a stable minimum.

Notice that the approach of [1] automatically gets rid of the double minimum, that allows to distinguish symmetric and antisymmetric states as the stretch modes with even and odd quantum numbers. Another approach was used in the paper of Traynor and Goodson [4], where the authors replaced nuclear part of the potential by a rescaled version

$$V_{\text{nucl}} = \left(1 + \frac{b}{D}\right)\frac{\zeta}{R}, \quad b = 3(\zeta^{-1} - 1). \tag{33}$$

It reduces to $1/R$ at physical dimensionality $D = 3$. By making the parameter ζ sufficiently small, one could force the effective potential to have only one global minimum.

In the two minima case, the splitting between symmetric and antisymmetric states could not recovered from the large-D limit. It was shown [9] that it could be estimated by WKB method by calculating tunneling probability along the most probable path in the (ρ, z) space.

VI. RELATIONSHIP BETWEEN LARGE-D LIMIT AND BOHR THEORY

It is easy to show that the ground state of D-dimensional hydrogen atom is equivalent to the lowest state of two-dimensional hydrogen atom having an angular momentum $m = (D-3)/2$ [10]. The density of probability for a two dimensional hydrogen atom corresponding to several values of D is shown on Fig. 4. Fig. 4 shows that the ground state for arbitrary D is equivalent to so-called *circular Rydberg state* in two dimensions. It is the lowest state for a

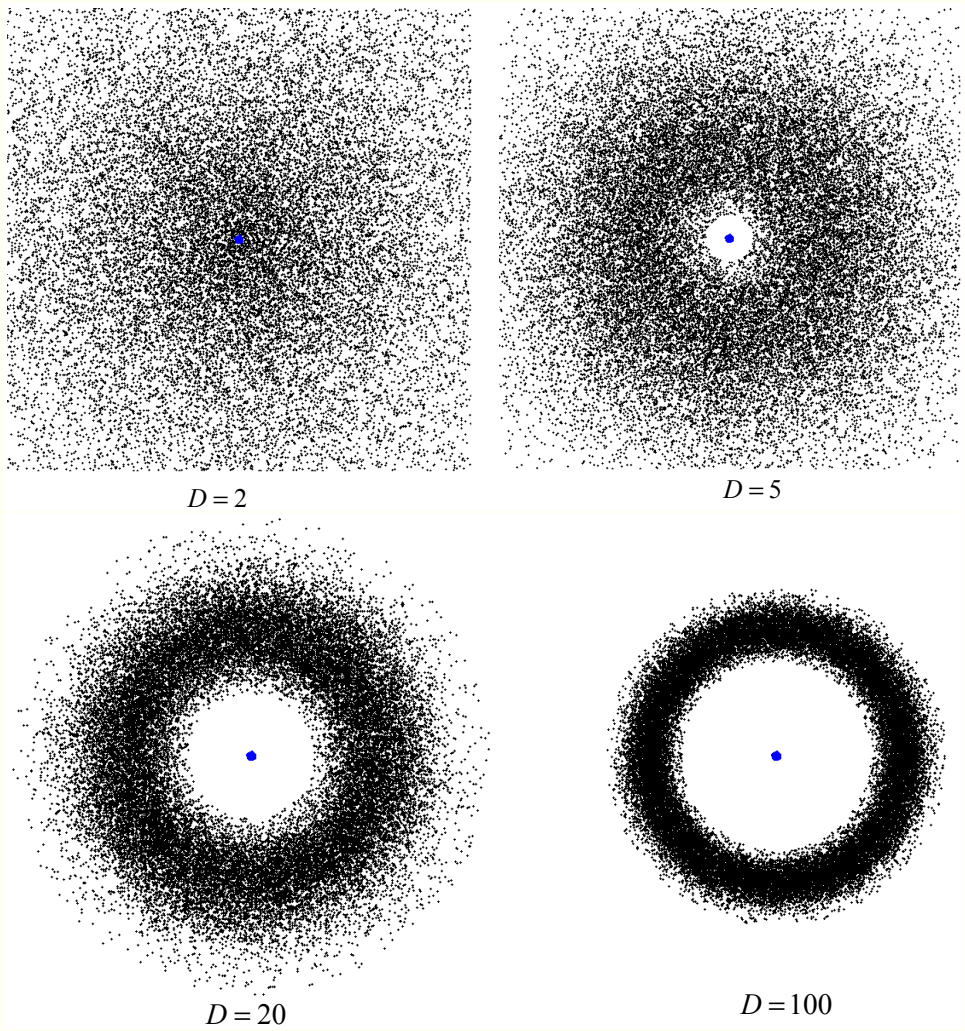

FIG. 4. Wave functions of two-dimensional hydrogen atom with angular momentum $m = D/2 - 1$ which is equivalent to the ground state of D-dimensional atom

given value of the angular momentum m. The limit of large D is equivalent to the limit of large m of the two-dimensional atom, when the quantum wave function approaches the classical circular orbit.

For the hydrogen molecular ion H_2^+, there exist a similar equivalence [7]. The ground state of H_2^+ in D dimensions is always equivalent to the lowest state in three dimensions, but with a non-zero angular momentum $L_z \equiv m = (D-2)/2$. Those states have wave functions concentrated along rings shown on Fig. 5.

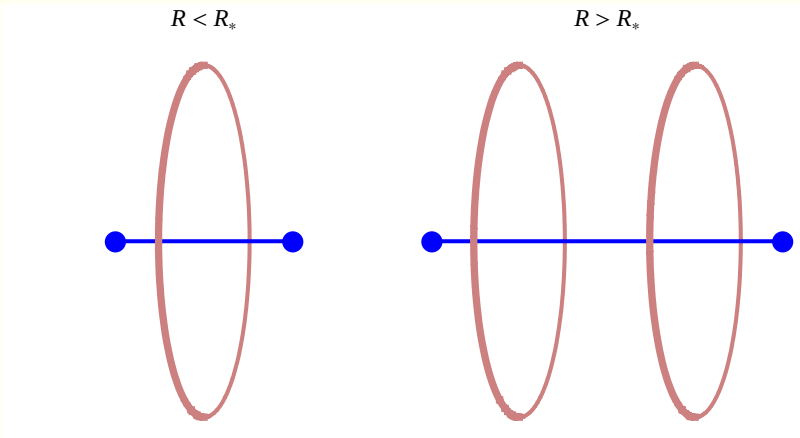

FIG. 5. Wave functions of high-m circular states of the hydrogen molecular ion

In the case of two electrons, there are similar equivalences (unpublished results). For example, the ground state of helium atom in D dimensions is equivalent to the lowest state of helium in *four* dimensions, but with a non-zero angular momentum, while the D-dimensional ground state of hydrogen molecule is equivalent to the lowest state of *five*-dimensional H_2 with non-zero momentum. In these cases, large-D limit corresponds to Bohr-like orbits of higher spacial dimensionality (larger than 3).

VII. BOHR MODEL FOR HYDROGEN MOLECULE

The large-D limit for a hydrogen molecule was systematically studied in the paper [7]. The potential for H_2 molecule is

$$V = -\frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}} + \frac{1}{R}, \tag{34}$$

where

$$r_{ia} = \left[\rho_i^2 + (z_i + R/2)^2\right]^{1/2}, \tag{35}$$

$$r_{ib} = \left[\rho_i^2 + (z_i - R/2)^2\right]^{1/2}, \tag{36}$$

$$r_{12} = \left[\rho_1^2 + \rho_2^2 - 2\rho_1\rho_2\cos\phi + (z_1 - z_2)^2\right]^{1/2}, \tag{37}$$

Fig. 6 shows the geometry of the molecule.

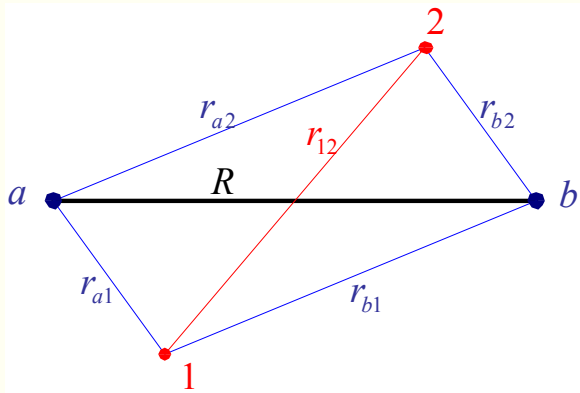

FIG. 6. Distances in H_2 molecule

Assuming that the wavefunction depends only on five variables, $\Psi = \psi(\rho_1, z_1, \rho_2, z_2, \phi)$, we finally arrive to a problem of finding a minimum in an effective potential

$$V_{\text{eff}}(\rho_1, z_1, \rho_2, z_2, \phi) = \frac{1}{2}\left(\frac{1}{\rho_1^2} + \frac{1}{\rho_1^2}\right)\frac{1}{\sin^2\phi} + V(\rho_1, z_1, \rho_2, z_2, \phi) \tag{38}$$

This minimum corresponds to a fixed geometrical configuration of electrons attained in large-D limit which is reminiscent of Lewis electron-dot structures of the earlier historical attempts to describe molecular bonds.

The energy as a function of separation distance is shown on Fig. 7. Again, in the large-D limit the molecule is unstable against dissociation because the curve is purely repulsive.

VIII. IMPROVING ACCURACY FOR THE GROUND STATE

The action of D-dimensional Laplacian $\boldsymbol{\nabla}_1^2 + \boldsymbol{\nabla}_2^2$ on the function of the form $\psi(\rho_1, z_1, \rho_2, z_2, \phi)$ may be represented as a sum of three differential operators,

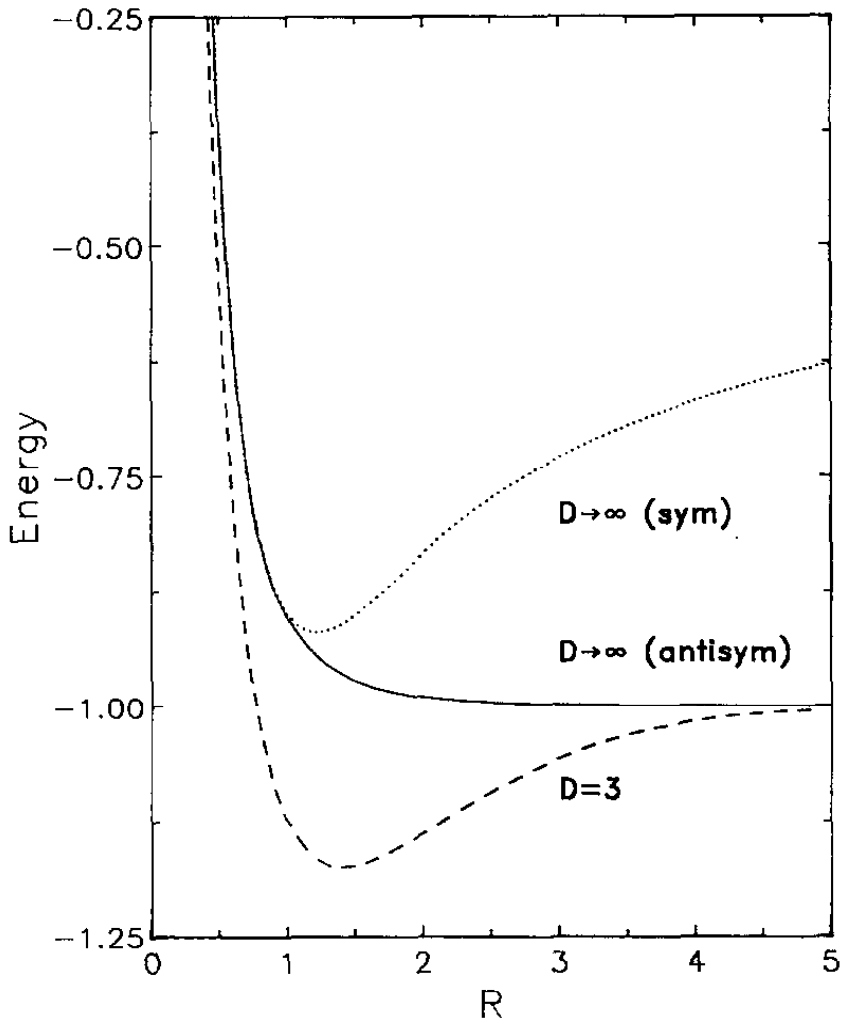

Fig. 11. Variation with R of H_2 total energies, sum of scaled electronic and nuclear repulsion terms. Solid and dotted curves pertain to $D \to \infty$ limit for the antisymmetric and symmetric case, respectively. Dashed curve is the $D=3$ ground-state total energy (ref. [8]).

FIG. 7. Ground state energy for H_2 molecule for $D = 3$ and in the large-D limit. The figure is taken from the paper [7]

T_ρ, T_z, and T_ϕ, where

$$T_\rho = \sum_i \frac{1}{\rho_i^{D-2}} \frac{\partial}{\partial \rho_i} \left(\rho_i^{D-2} \frac{\partial}{\partial \rho_i} \right), \tag{39}$$

$$T_z = \sum_i \frac{\partial}{\partial z_i^2}, \tag{40}$$

$$T_\phi = \left(\frac{1}{\rho_1^2} + \frac{1}{\rho_2^2} \right) \frac{1}{\sin^{D-3}\phi} \frac{\partial}{\partial \phi} \left(\sin^{D-3}\phi \frac{\partial}{\partial \phi} \right). \tag{41}$$

The novel method proposed in papers [2, 3] is based on the observation that if we introduce an alternative operator

$$T'_\phi = \left(\frac{1}{\rho_1^2} + \frac{1}{\rho_2^2} \right) \frac{\partial}{\partial \phi} \left(\frac{\partial}{\partial \phi} \right), \tag{42}$$

then obviously $T'_\phi = T_\phi$ in case of physical dimensionality $D = 3$. This fact allows to consider a hypothetical system described by the Schrödinger equation in which T_ϕ is replaced by T'_ϕ,

$$\left(T_\rho + T_z + T'_\phi + V(\rho_1, z_1, \rho_2, z_2, \phi) - E' \right) \psi(\rho_1, z_1, \rho_2, z_2, \phi) = 0. \tag{43}$$

In equation (43), E' depends on dimensionality in a different way in comparison with E. However, for the physical case of $D = 3$, both functions are the same. Since the operator T'_ϕ does not depend on D at all, we could expect that the large-D limit of the equation (43) is closer to $D = 3$ case than the corresponding limit of the true D-dimensional generalization that contains the operator T_ϕ which *depends* on D.

This approach, after scaling of variables, leads to finding a minimum of the following effective potential,

$$V'_{\text{eff}}(\rho_1, z_1, \rho_2, z_2, \phi) = \frac{1}{2} \left(\frac{1}{\rho_1^2} + \frac{1}{\rho_1^2} \right) + V(\rho_1, z_1, \rho_2, z_2, \phi) \tag{44}$$

The potential in equation (44) differs from those in equation (38) only by absence of $\sin^2\phi$ in the denominator of the positive centrifugal energy. Thus,

$V'_{\rm eff}$ is always smaller than $V_{\rm eff}$ for the same arguments. We could expect that the resulting energy will be lower. Calculations confirm that the accuracy improves. The dependence on R is shown on Fig. 8. The most important improvement is the appearance of a minimum on the curve, meaning the stability of the limit $D \to \infty$.

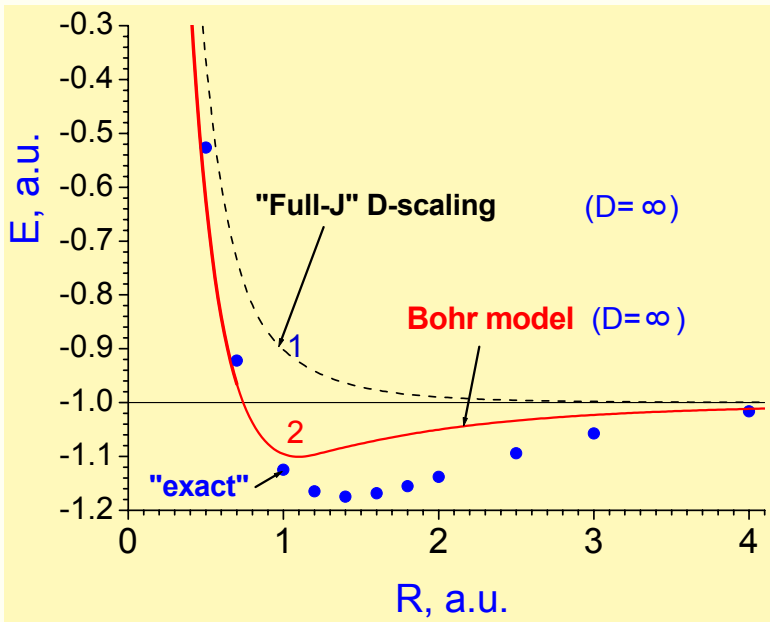

FIG. 8. Ground state energy for H_2 molecule for $D = 3$ and in the large-D limit for two different choices of D-dimensional generalization of the problem. Dashed curve is the true large-D limit, also shown as solid line on Fig. 7. Solid line No. 2 is the large-D limit of the alternative generalization of the problem given by equation (43). Notice that the curve has a minimum corresponding to stable equilibrium separation distance.

Results obtained by including $1/D$ correction, $E(D \to \infty) + E_1 D^{-1}$, are shown on Fig. 9. Surprisingly, the accuracy deteriorates.

There was proposed an alternative ad hoc method of taking into account finite-D corrections. The method consists of solving one-dimensional Schrödinger equation numerically in the direction of stretching-mode vibrations and adding this energy to the large-D limit. It allows to eleminate pathological cusp-like behavior near the point where the minimum along the

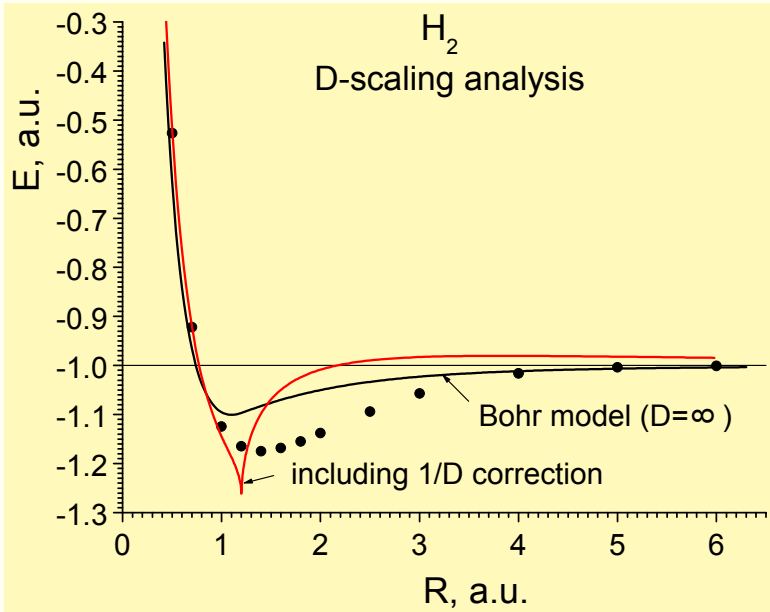

FIG. 9. Ground state energy for H_2 molecule obtain without and with $1/D$ correction within alternative D-generalization.

stretch mode dissapears. The results are shown on Fig. 10.

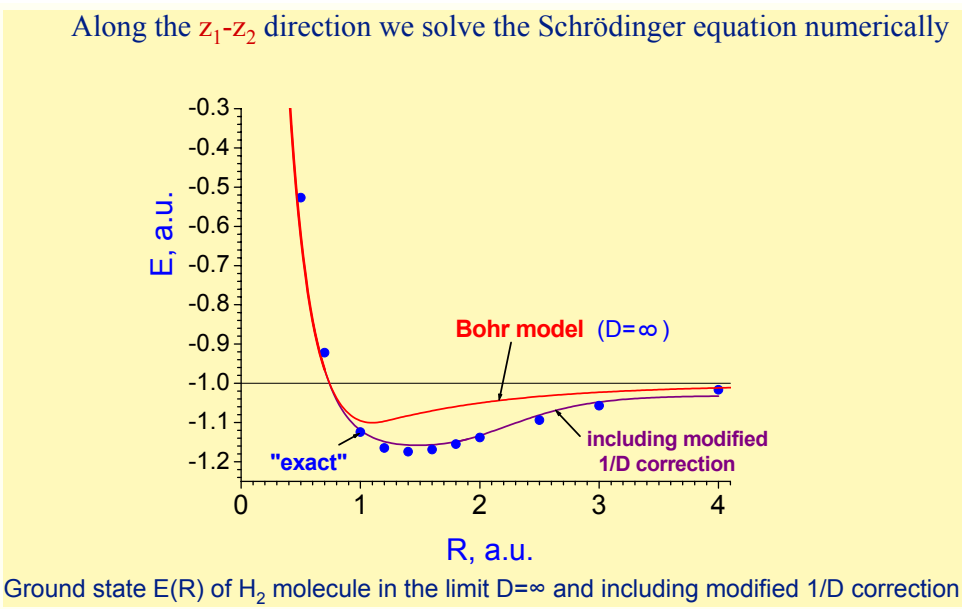

FIG. 10.

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