

Bohr's 1913 molecular model revisited

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It is generally believed that the old quantum theory, as presented by Niels Bohr in 1913, fails when applied to few electron systems, such as the H₂ molecule. Here, we find previously undescribed solutions within the Bohr theory that describe the potential energy curve for the lowest singlet and triplet states of H₂ about as well as the early wave mechanical treatment of Heitler and London. We also develop an interpolation scheme that substantially improves the agreement with the exact ground-state potential curve of H₂ and provides a good description of more complicated molecules such as LiH, Li₂, BeH, and He₂.

Bohr model | chemical bond | molecules

The Bohr model (1–3) for a one-electron atom played a major historical role and still offers pedagogical appeal. However, when applied to the simple H₂ molecule, the “old quantum theory” proved unsatisfactory (4, 5). Here we show that a simple extension of the original Bohr model describes the potential energy curves $E(R)$ for the lowest singlet and triplet states about as well as the first wave mechanical treatment by Heitler and London (6).

We find the Bohr model of H₂ admits other solutions than the symmetric one he considered (pictured in Fig. 1).^{||} These solutions provide a fairly good description of the ground-state $E(R)$ (see curve 2 in Fig. 3) at large as well as small internuclear spacing R , in contrast with the result of Bohr (see curve 1 in Fig. 3).

Clearly, the Bohr picture of a molecule goes wrong at large R . Any realistic model must show the ground-state potential energy function dissociating to H + H. Sommerfeld, in his seminal book (5), provided the following apt assessment: “We shall now describe a little more fully the model that Bohr has suggested for the constitution of the hydrogen molecule H₂, although, nowadays, we can take only a historical interest in it.” After some discussion, he asks, “But is it correct?” To which he answers, “Only a short while ago, even while this book was in its first edition, we were inclined to accept it.” And later he concludes, “Thus the true model of the H₂ molecule is still unknown. It will hardly be as symmetrically built as the model exhibited in [figure] 22.” His figure 22 is the same as our symmetric configuration in Fig. 3.

It is somewhat ironic that the Bohr picture of the molecule never caught on. As with the Bohr atomic picture, it contains valuable insight and can provide a good analytical description of molecular behavior. Sommerfeld even sensed that the symmetric configuration was suspect. In Fig. 3, we present a simple continuation of the line of thought that Bohr was following, which is indeed asymmetric and provides a good quantitative picture of H₂ at small and large R . We next outline Bohr's insightful picture and our extensions.

Fig. 2 displays the Bohr model for a hydrogen molecule, in which two nuclei with charges $Z|e|$ are separated by a fixed distance R (adiabatic approximation), and the two electrons move in the space between them. The model assumes that the electrons move with constant speed on circular trajectories of radii $\rho_1 = \rho_2 = \rho$. The circle centers lie on the molecule axis z at the coordinates $z_1 = \pm z_2 = z$. The separation between the electrons is constant. The net force on each electron consists of

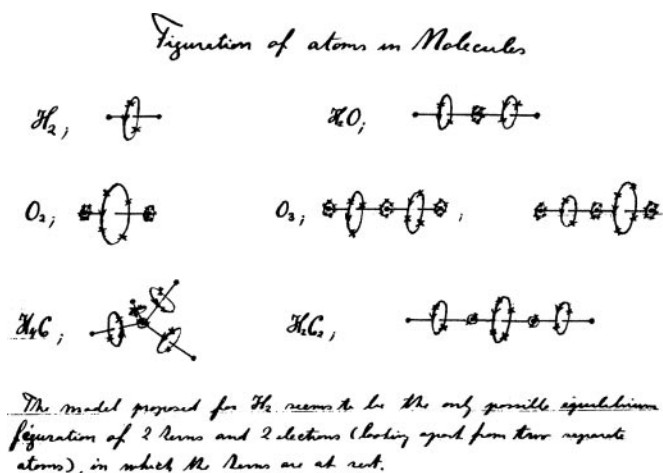


Fig. 1. Molecular configurations as sketched by Niels Bohr; [from an unpublished manuscript (7), intended as an appendix to his 1913 papers]. [Reprinted with permission from ref. 7 (Copyright 1981, Elsevier).]

the following three contributions: attractive interaction between an electron and the two nuclei, the Coulomb repulsion between electrons, and the centrifugal force on the electron. We proceed by writing the energy function $E = T + V$, where the kinetic energy $T = p_1^2/2m + p_2^2/2m$ for electrons 1 and 2 can be obtained from the quantization condition that the circumference is equal to the integer number n of the electron de Broglie wavelengths $2\pi\rho = nh/p$, so that we have $T = p^2/2m = n^2\hbar^2/2m\rho^2$. All distances we express in terms of the Bohr length $a_0 = \hbar^2/me^2$, where m is the electron mass, and take e^2/a_0 as a unit of energy. The Coulomb potential energy V is given by

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

where r_{ai} ($i = 1, 2$) and r_{bi} are the distances of the i th electron from nuclei A and B , as shown in Fig. 2 Lower, and r_{12} is the separation between electrons. In cylindrical coordinates the distances are

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

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

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Abbreviation: a.u., atomic unit.

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^{||}In response to a referee who said, “[I]t is hard to believe that Bohr and his students were not aware of the other solutions,” we researched the issue further. In fact, Bohr says the following in his handwritten notes (7): “The model proposed for H₂ seems to be the only possible equilibrium figuration of 2 nuclei and 2 electrons (looking apart from two separate atoms), in which the kernels are at rest.” Furthermore, Sommerfeld (5) was clearly unaware of the key asymmetric configuration of Fig. 2.

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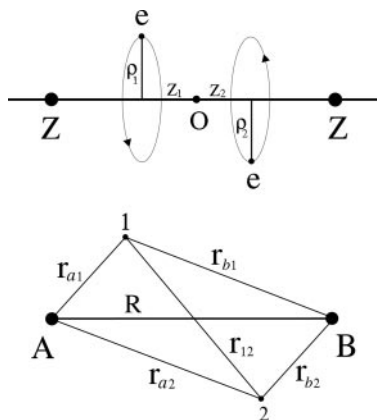


Fig. 2. Cylindrical coordinates (*Upper*) and electronic distances (*Lower*) in H_2 molecule. The nuclei Z are fixed at a distance R apart. The two electrons rotate about the internuclear axis z with coordinates ρ_1, z_1 and ρ_2, z_2 , respectively; the dihedral angle ϕ between the (ρ_1, z_1) and (ρ_2, z_2) planes remains constant at either $\phi = \pi$ or $\phi = 0$. The sketch corresponds to configuration 2 of Fig. 3, with $\phi = \pi$.

where R is the internuclear spacing and ϕ is the dihedral angle between the planes containing the electrons and the internuclear axis. The Bohr model energy for a homonuclear molecule having charge Z is then given by (here we discuss the case $n = 1$)

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

Possible electron configurations correspond to extrema of Eq. 2. There are four such configurations for which $\rho_1 = \rho_2 = \rho$, $z_1 = \pm z_2 = z$, and $\phi = \pi, 0$; they are depicted in Fig. 3 *Upper*.

In Fig. 3 *Lower*, we plot $E(R)$ for the four Bohr model configurations (solid curves), together with “exact” results (dots) obtained from extensive variational wave mechanical calculations for the singlet ground state, $^1\Sigma_g^+$, and the lowest triplet state, $^3\Sigma_u^+$ (for a good overview of modern molecular theory, see ref. 8). In the model, the three configurations 1, 2, 3 with the electrons on opposite sides of the internuclear axis ($\phi = \pi$) are seen to correspond to singlet states, whereas the other solution 4 with the electrons on the same side ($\phi = 0$) corresponds to the triplet state. At small internuclear distances, the symmetric configuration 1 originally considered by Bohr agrees well with the exact ground-state quantum energy; at larger R , however, this configuration climbs far above the ground state and ultimately dissociates to the doubly ionized limit, $2H^+ + 2e$. In contrast, the solution for the asymmetric configuration 2 appears only for $R > 1.20$ and in the large R limit dissociates to two H atoms. The solution for asymmetric configuration 3 exists only for $R > 1.68$ and climbs steeply to dissociate to an ion pair, $H^+ + H^-$. The asymmetric solution 4 exists for all R and corresponds throughout to repulsive interaction of the two H atoms.

The simplistic Bohr model provides surprisingly accurate energies for the ground singlet state at large and small internuclear distances and for the triplet state over the full range of R . Also, the model predicts the ground state is bound with an equilibrium separation $R_e \approx 1.10$ and gives the binding energy as $E_B \approx 0.100$ atomic units (a.u.) = 2.73 eV (1 eV = 1.602×10^{-19} J). The Heitler–London calculation, obtained from a two-term variational function, obtained $R_e = 1.51$ and $E_B = 3.14$ eV (4), whereas the exact results are $R_e = 1.401$ and $E_B = 4.745$ eV (ref. 8; for a good treatment of the Kohn–Hohenberg–Sham density functional theory, see ref. 9). For the triplet state, as seen in Fig. 3, the Bohr model gives remarkably close agreement with the exact potential curve and is in fact much better than the Heitler–London result (which,

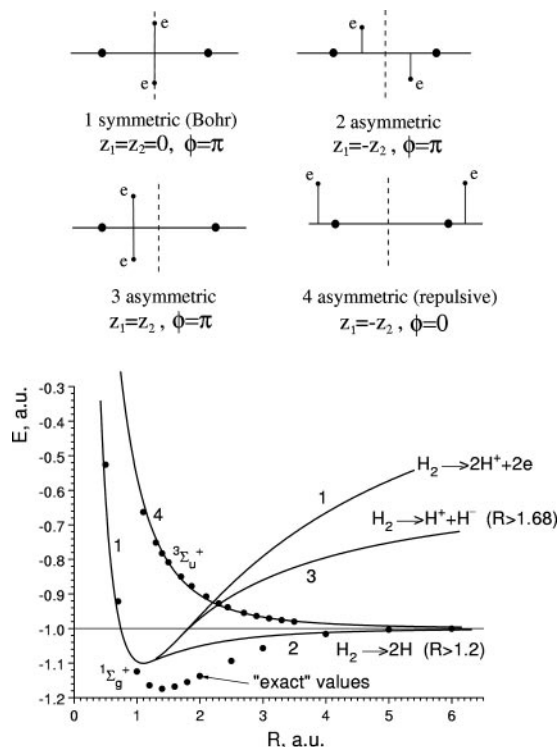


Fig. 3. Energy $E(R)$ of H_2 molecule for four electron configurations (*Upper*) as a function of internuclear distance R calculated within the Bohr model (solid lines) and the exact ground $^1\Sigma_g^+$ and first excited $^3\Sigma_u^+$ state energy (dots).** Unit of energy is 1 atomic unit (a.u.) = 27.21 eV, and unit of distance is the Bohr radius. Please note a similarity between the symmetric configuration 1 and Bohr’s sketch of H_2 molecule in Fig. 1.

e.g., is 30% high at $R = 2$). One should mention that in 1913, Bohr found only the symmetric configuration solution, which fails drastically to describe the ground-state dissociation limit. Although a variety of modifications were later considered (4, 10), to our knowledge the other three solutions of the simplest model have never been discussed in the literature. One should certainly pay tribute to Bohr’s planetary model proposed long before the development of quantum mechanics. It is somewhat ironic that the Bohr model can be derived from quantum mechanics in the limit of large dimensions (11).

We conclude this first portion of this work with a quick sketch of the way the calculations are carried out to emphasize how

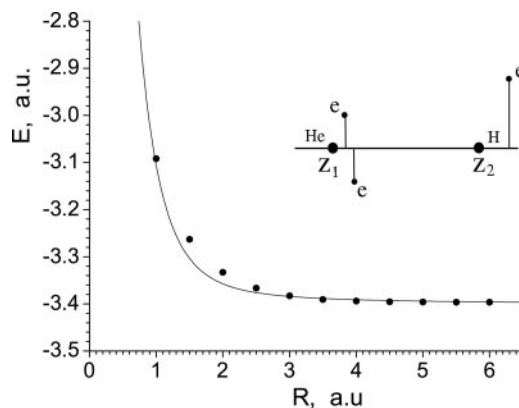


Fig. 4. Energy $E(R)$ of HeH molecule for the shown electron configuration calculated within the Bohr model for $n_1 = n_2 = n_3 = 1$, $Z_{He}^{eff} = 1.954$ (solid line) and the exact ground-state energy (dots).

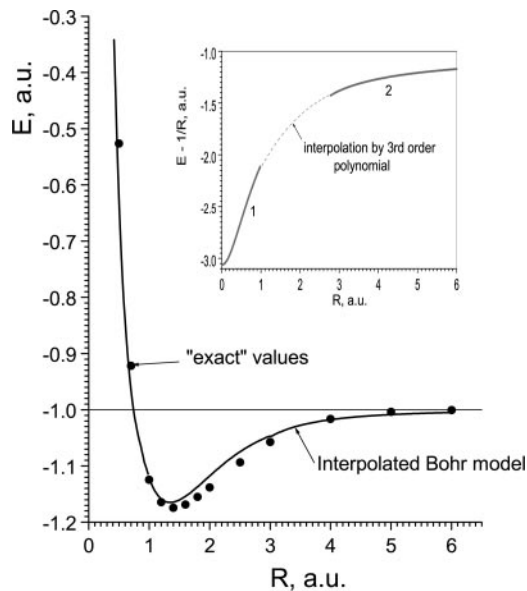


Fig. 5. Ground-state $E(R)$ of H_2 molecule calculated within the interpolated Bohr model (solid line) and the exact energy (dots). ** Inset shows $E(R)$ with no $1/R$ term. Curves 1 and 2 are obtained based on the quantization relative to the molecular axis (small R) and the nearest nuclei (large R), respectively. Dashed line represents the interpolation between two regions.

simple the present analysis is, as compared with the many-particle Schrödinger equation. For example, for the configuration 2, with $z_1 = -z_2 = z$, $\phi = \pi$, the extremum equations $\partial E/\partial z = 0$ and $\partial E/\partial \rho = 0$ read

$$\frac{Z(R/2 - z)}{[\rho^2 + (R/2 - z)^2]^{3/2}} + \frac{z}{4[\rho^2 + z^2]^{3/2}} - \frac{Z(R/2 + z)}{[\rho^2 + (R/2 + z)^2]^{3/2}} = 0, \quad [3]$$

$$\frac{Z\rho}{[\rho^2 + (R/2 - z)^2]^{3/2}} + \frac{Z\rho}{[\rho^2 + (R/2 + z)^2]^{3/2}} - \frac{\rho}{4[\rho^2 + z^2]^{3/2}} = \frac{1}{\rho^3}, \quad [4]$$

which are seen to be equivalent to Newton's second law applied to the motion of each electron. Eq. 3 specifies that the total Coulomb force on the electron along the z -axis is equal to zero; Eq. 4 specifies that the projection of the Coulomb force toward the molecular axis equals the centrifugal force. At any fixed internuclear distance R , these algebraic equations determine the

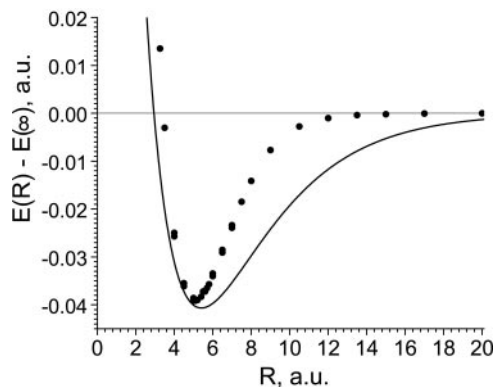


Fig. 6. Ground-state energy $E(R)$ of Li_2 molecule calculated within the interpolated Bohr model (solid line) and the exact energy (dots).

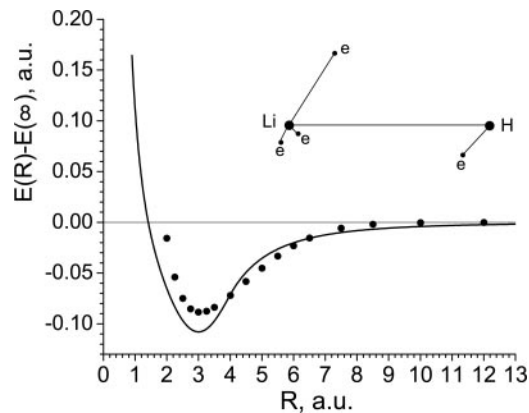


Fig. 7. Electron configuration and the ground-state energy $E(R)$ of LiH molecule as a function of internuclear distance R calculated within the interpolated Bohr model (solid line) and the exact energy (dots).

constant values of ρ and z that describe the electron trajectories. Substituting these values back into Eq. 2 yields $E(R)$. Similar force equations describe the other extremum configurations.

The simple Bohr model is also useful in describing more complicated diatomic molecules. For N electrons the model reduces to finding configurations that deliver extrema of the energy

$$E = \frac{1}{2} \sum_{i=1}^N \frac{n_i^2}{\rho_i^2} + V(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N, R). \quad [5]$$

In such a formulation of the model, there is no need to specify electron trajectories and also incorporate nonstationary electron motion. One can obtain the energy function (Eq. 5) from dimensional scaling analysis of the Schrödinger equation in large-D limit (11). This analysis provides a link between the old (Bohr-Sommerfeld) and the new (Heisenberg-Schrödinger) quantum mechanics.

Next, we discuss the ground-state potential curve of HeH . To incorporate the Pauli exclusion principle, one can use a prescription based on the sequential filling of the electron levels. In the case of HeH , the three electrons cannot occupy the same lowest level of HeH^{++} . Therefore, for the configuration with $n_1 = n_2 = n_3 = 1$, the true ground-state energy corresponds to a saddle point rather than to a global minimum. Such a configuration is pictured in Fig. 4 Inset. To obtain the correct dissociation limit, we assign the helium nucleus an effective charge $Z_{He}^{eff} = 1.954$. Fig. 4 shows the ground-state potential curve of HeH in the Bohr model (solid curve) and the exact result (dots) obtained from extensive variational wave mechanical calculations. ** The Bohr model gives remarkably close agreement with the exact potential energy curve.

We have found a simple means to improve significantly the Bohr model results for bound electronic states. The original model assumes quantization of the electron angular momentum relative to the molecular axis. As seen in Fig. 3, this quantization yields a quite accurate description of the H_2 ground-state $E(R)$ at small R but becomes less accurate at larger internuclear separation. An improvement emerges from the following observation. At large R each electron in H_2 feels only the nearest nuclear charge. Accordingly, as $R \rightarrow \infty$, we have two weakly interacting, neutral H atoms. Therefore, at large R , quantization of the momentum relative to the nearest nuclei, rather than to the molecular axis, yields a better

**Throughout this work, exact energies (solid dots) are taken from a combination of experimental and theoretical sources. The theoretical analyses are typically many-term (10–100) configuration interaction computer calculations (see, for example, ref. 8).

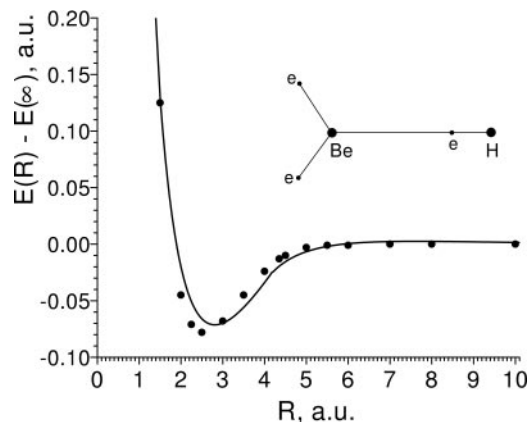


Fig. 8. Ground-state energy $E(R)$ of BeH molecule calculated within the interpolated Bohr model (solid line) and the exact energy (dots). *Inset* shows the electron configuration at large R ; only outer shell Be electrons are displayed.

description of the physics. This technique leads to the following expression for the energy of the H_2 molecule:

$$E = \frac{1}{2} \left(\frac{n_1^2}{r_{a1}^2} + \frac{n_2^2}{r_{b2}^2} \right) + V(r_{a1}, r_{b1}, r_{a2}, r_{b2}, r_{12}, R). \quad [6]$$

For $n_1 = n_2 = 1$ and $R > 2.8$, the expression in Eq. 6 has a local minimum for the asymmetric configuration 2 of Fig. 3. We plot the corresponding $E(R)$ without the $1/R$ term in the insert of Fig. 5 (curve 2). At $R < 2.8$ the local minimum disappears and electrons collapse into the opposite nuclei. At small R we apply the quantization condition relative to the molecular axis which yields the curve 1 in Fig. 5. To find $E(R)$ at intermediate separation we smoothly connect the two regions by a third-order polynomial (dashed line). Addition of the $1/R$ term yields the final potential curve, plotted in Fig. 5. This simple interpolated Bohr model provides good agreement with the exact potential curve over the full range of R .

Next, we consider the Li_2 molecule. If we neglect inner shell electrons of Li, then the Li_2 molecule becomes similar to an excited state of H_2 with $n_1 = n_2 = n = 2$ in Eq. 6. Rescaling coordinates in Eq. 6 as $r \rightarrow n^2 r$, $R \rightarrow n^2 R$ yields the energy function

$$E = \frac{1}{n^2} \left\{ \frac{1}{2r_{a1}^2} + \frac{1}{2r_{b2}^2} + V(r_{a1}, r_{b1}, r_{a2}, r_{b2}, r_{12}, R) \right\}. \quad [7]$$

Hence, the ground-state potential curve of Li_2 can be obtained from the ground-state $E(R)$ of H_2 by using the following relation:

$$E_{Li_2}(R) - E_{Li_2}(\infty) = \frac{1}{n^2} [E_{H_2}(n^2 R) - E_{H_2}(\infty)]. \quad [8]$$

The result is shown in Fig. 6 (solid line). For Li_2 the Bohr model gives the binding energy $E_B = 1.10$ eV, which is very close to the exact value of $E_B = 1.05$ eV.

As an example of application of the extended Bohr model to other diatomic molecules, we discuss the ground-state $E(R)$ of LiH. The Li atom contains three electrons, two of which fill the inner shell. Only the outer electron with the principal quantum

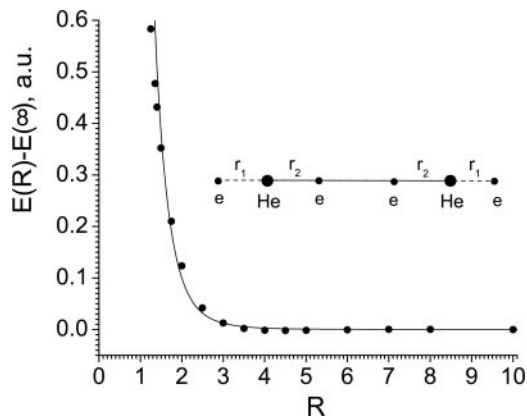


Fig. 9. Ground-state energy $E(R)$ of He_2 molecule calculated within the Bohr model (solid line) and the exact energy (dots). *Inset* shows the electron configuration.

number $n = 2$ is important in formation of the molecular bond. Applying a similar approach to that used to obtain Fig. 5, we find $E(R)$ for LiH as shown in Fig. 7 (solid line), while dots are the exact numerical answer. This simple extension of the Bohr model provides a good quantitative description of the LiH potential curve. In this treatment, the essential difference from H_2 arises simply because in LiH the $n = 2$ electron from Li is much more weakly bound than the $n = 1$ electron from H, with the result that for LiH the binding energy is 2-fold less than for H_2 , and the equilibrium separation is roughly twice as large. As seen in Fig. 8, the same procedure also gives a good potential curve for BeH, a relatively complex five-electron system.

Finally, we show how our very simple analysis yields very accurate potential curve for the He_2 molecule. We apply the Bohr model with momentum quantization relative to the nearest nuclei and assume the electron configuration as shown in Fig. 9 *Inset*. Then the problem reduces to finding minimum of the following energy function:

$$E = \frac{1}{r_1^2} + \frac{1}{r_2^2} - \frac{2Z}{r_1} - \frac{2Z}{r_2} + \frac{2}{r_1 + r_2} + \frac{2}{R + r_1 - r_2} + \frac{1}{R + 2r_1} + \frac{1}{R - 2r_2} + \frac{Z^2}{R}. \quad [9]$$

Minimization of this simple expression at fixed R leads the potential energy curve pictured in Fig. 9 (solid line). The curve essentially passes through the exact dots over the full range of R .

In conclusion, we find a simple extension of the Bohr molecular model that gives a clear physical picture of how electrons create chemical bonding. At the same time, the description is surprisingly accurate, providing good potential energy curves for relatively complex many body systems.

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