Model of molecular bonding based on the Bohr-Sommerfeld picture of atoms

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We develop a model of molecular bonding based on the Bohr-Sommerfeld description of atoms together with a constraint taken from conventional quantum mechanics. The model can describe the binding energy curves of \( \text{H}_2 \), \( \text{H}_3 \) and other molecules with striking accuracy. Our approach treats electrons as point particles with positions determined by extrema of an algebraic energy function. Our constrained model provides a physically appealing, accurate description of multi-electron chemical bonds.

Quantum chemistry has achieved excellent agreement between theory and experiment by use of computational power to provide an adequate description electron-electron interactions. The conventional treatment of molecular structure are based on solving the many-particle Schrödinger equation with varying degree of sophistication, ranging from Diffusion Monte Carlo methods, coupled cluster expansion, configuration interactions, to density functional theory. All are intensely numerical, limited to rather small systems and at the expense of providing a simple physical picture of the chemical bond. Despite the successes of modern computational chemistry, there remains a need for understanding electron correlations in some relatively simple way so that we may describe ground and excited states of large systems with reasonable accuracy.

Our goal here is to advance an intuitively appealing model of molecular bonding capable of producing binding energy curves at chemical accuracy of a few milli-Hartree. Our approach is based on the recently resurrected Bohr’s 1913 model for molecules, which is derivable from an infinite dimensional reduction of the Schrödinger equation. The resulting electron configurations are reminiscent of the Lewis electron-dot structure introduced in 1916. The surprising feature of our work is that all molecular binding energy curves studied below can be accounted for by mostly electrostatic interaction of “well-placed” electrons, as if all the complicated kinetic and overlapping integrals have been approximated by their mean-values via well-chosen electron positions. Such an approach can potentially describe the structural elements of large molecules beyond the current capability of ab initio methods.

We will first derive our model for \( \text{H}_2 \), followed by applications to more complex molecules. Fig. 1 displays various electron distances in \( \text{H}_2 \). Distances and energies are in units of the Bohr radius \( a_0 = (\hbar^2/m_e e^2) \) and Hartree \( = e^2/a_0 \) respectively. The original molecular Bohr model quantize the electron’s angular momentum about the molecular axis resulting in the ground state energy function,

\[
E = \frac{1}{2} \left( \frac{1}{\rho_1^2} + \frac{1}{\rho_2^2} \right) + V, \tag{1}
\]

where the first term is the Bohr kinetic energy and \( V \) is the Coulomb potential energy given in terms of electron distances defined in Fig. 1.

\[
V = -\frac{1}{r_1} - \frac{1}{r_2} - \frac{1}{r_{12}} - \frac{1}{r_{12}} + \frac{1}{R}, \tag{2}
\]

\( R \) is the internuclear separation. In our model, electron configurations of a physical state correspond to extrema of an energy function, such as Eq. 1.

In Fig. 2 (curve 1) we plot the ground state \( E(R) \) of Eq. 1, together with “exact” quantum mechanical results (solid circles). The original Bohr model yields a fairly accurate \( \text{H}_2 \) ground state energy \( E(R) \) at small \( R \), but becomes increasingly inaccurate at larger internuclear separations. This can be remedied by the following observation. At large \( R \) each electron in \( \text{H}_2 \) feels only the nearest nuclear charge, resulting in two weakly interacting neutral \( \text{H} \) atoms. Therefore, at large \( R \) each electron’s angular momentum ought to be quantized relative to the nearest nucleus, rather than to the molecular axis. This asymptotic consideration yields the following \( \text{H}_2 \) energy

\[
E = \frac{1}{2} \left( \frac{1}{r_1} + \frac{1}{r_2} \right) + V. \tag{3}
\]

For \( R > 2.77 \) this energy function has a local minimum for the top configuration of Fig. 1. We plot the corresponding \( E(R) \) in Fig. 2 (curve 2). However, at \( R < 2.77 \) the local minimum of the energy function disappears.
and each electron can collapse onto the other nucleus, i.e., \( r_{b1} \) and/or \( r_{b2} \) can vanish. As one can see from Fig. 2, the energy function \( \Phi \), which is a natural generalization of Bohr’s hydrogen atom to the molecular case, is in good quantitative agreement with the “exact” energy over the range of \( R > 2.77 \) where the local minimum exists. This encourages us to seek a way of extending the applicability of Eq. (3) to the entire range of \( R \).

In the above naive generalization of Bohr’s atom to the molecular case, each electron can collapse onto the other nucleus because there is no corresponding Bohr kinetic energy term about that nucleus to prevent the collapse. By incorporating further insights from quantum mechanics, we can remove this instability by a simple constraint. Quantum mechanically, the two electrons are described by a wave function \( \Psi(r_1, r_2) \). Electron 1 is a charge cloud with a most probable radius \( r \). Let

\[
\Phi(r, R) \equiv \left\langle \Psi \left| -\frac{1}{r_{b1}} \right| \Psi \right\rangle
\]  

be the quantum mechanical potential between the electron cloud centered at nucleus A and the nuclear charge of B, or vice versa. In the Bohr picture we treat the electron as a point particle on a sphere of radius \( r \) centered about nucleus A. A subset of the spherical surface, a “circle” of positions \( r \) satisfying

\[
-\frac{1}{r_{b1}} = \Phi(r, R)
\]

will give the correct quantum mechanical interaction energy with nucleus B. Thus if we impose the above as a constraint, and choose the electron location only from this subset of the positions, then \( r_{b1} \) can never be zero, because the expectation value in Eq. 4 is finite.

One can derive the effective potential \( \Phi(r, R) \) from any simple two-electron wave functions, such as the Heitler-London (HL) or the Hund-Mulliken (HM) wave function \( \Psi \). The HL wave function is

\[
\Psi = a(1)b(2) \pm b(1)a(2),
\]

where “+/-” corresponds to singlet/triplet state and

\[
a(i) = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha r_i), \quad b(i) = \sqrt{\frac{\alpha^3}{\pi}} \exp(-\alpha r_i),
\]

for \( i = 1 - 2 \) are variational wave functions with parameter \( \alpha \). If we take \( a(1) \) as a variational wave function for an isolated hydrogen atom, then the variational energy is \( E = \alpha^2/2 - \alpha \). This reduces to the Bohr model energy function for the hydrogen atom if we identify \( \alpha = 1/r \), where \( r \) is the radial distance from the nucleus. We will also use \( r \) to denote the radial distance of an electron from its nearest nucleus.

For the HL wave function Eq. (4) yields the well known Coulomb and exchange integral,

\[
\Phi = -\frac{1}{1 + S^2} \left\{ \int \frac{a^2(1)}{r_{b1}} \Psi_1 + 2S \int a(1)b(1) \frac{1}{r_{b1}} \Psi_1 \right\},
\]

with overlap \( S = \int a(1)b(1) \Psi_1 \). More explicitly, the singlet and triplet potentials are respectively

\[
\Phi_s(r, R) = -\frac{1}{1 + S^2(r, R)} \left[ f(r, R) + S(r, R) g(r, R) \right],
\]

\[
\Phi_t(r, R) = -\frac{1}{1 - S^2(r, R)} \left[ f(r, R) - S(r, R) g(r, R) \right],
\]

with \( f(r, R) = 1/R - \exp(-2R/r) (1/r + 1/R), \) \( g(r, R) = \exp(-R/r)(1 + R/r)/r \) and

\[
S(r, R) = \exp(-R/r) \left( 1 + \frac{R}{r} + \frac{R^2}{3r^2} \right).
\]

The singlet state Hund-Mulliken wave function \( \Psi = [a(1) + b(1)] [a(2) + b(2)] \) yields the HM singlet effective potential:

\[
\Phi_s(r, R) = -\frac{1}{1 + S(r, R)} \left[ f(r, R) + g(r, R) \right].
\]

For the triplet state, the HL and HM wave functions are the same, yielding identical triplet potentials. Note that by introducing singlet and triplet potentials, we have augmented the original atomic Bohr model with elements of Pauli’s exclusion principle. The latter is essential for any successful description of atomic and molecular systems.

When we apply the constrained Bohr model to \( \mathrm{H}_2 \), the resulting energy function is

\[
E(r, R) = \frac{1}{r^2} - \frac{2}{r} + 2\Phi(r, R) + \frac{1}{r_{12}} + \frac{1}{R}.
\]
shown in Fig. 3, where, for singlet ground state corresponding to the ground and triplet states are as shown in Fig. 4 where, for singlet ground state

\[ r_{12} = \sqrt{2r^2 - R^2 + \frac{2}{\Phi^2(r, R)}}. \]

and for the triplet excited state,

\[ r_{12} = \frac{1}{R\Phi^2(r, R)} - \frac{r^2}{R}. \]

These are just geometric distances between the two electrons expressed in terms of \( R, r \) and \( r_{12} \). The angle \( \theta \) is determined by the relation \( 1/\Phi^2 = R^2 + r^2 - 2rR \cos \theta \).

The binding energy curves \( E(R) \) for both singlet and triplet states are shown in Fig. 4. There are no fitting parameters in our calculations. The solid and dotted lines are results from using the HM and HL potential respectively. Solid circles are “exact” results [7]. The constrained Bohr model gives a surprisingly accurate \( E(R) \) at all \( R \), yielding a ground state binding energy of \( E_B = 4.50 \) eV for the HL potential and \( E_B = 4.99 \) eV for the HM potential [10]. The “exact” result is \( E_B = 4.745 \) eV [1]. The Heitler-London-Wang effective charge calculation (dashed curves) gives substantially worse accuracy with \( E_B = 3.78 \) eV [8, 11]. Only more elaborate variational calculations with configuration interaction can produce energies comparable to our constrained Bohr model results.

Generalizing the constraint Eq. (5) to a system of several hydrogen atoms is straightforward. Let’s consider electron 1 belonging to its nearest nucleus 1 and denote the distances from electron 1 to nuclei \( i \) as \( r_i \) (\( i = 1, 2, \ldots \)). Then the constraint equation reads

\[ -\sum_{i>1} \frac{1}{r_i} = \sum_{i>1} \Phi_i(r_1, R_i), \quad \text{Eq. (13)} \]

where \( R_i \) is the separation between nucleus 1 and nucleus \( i \). Mutual spin orientation of electrons 1 and electron \( i \) (belonging to nucleus \( i \)) determines a singlet or triplet \( \Phi_i \) in Eq. (13). In this way, we have incorporated elements of Pauli’s exclusion principle into our model.

When applying our model to the triatomic \( \text{H}_3 \) molecule, we consider linear and triangular configurations as shown in the insert of Figs. 5 and 6. The spacing between the nearest nuclei is assumed to be the same, equal to \( R \). Due to symmetry, the central electron in the linear \( \text{H}_3 \) molecule must be at equal distances from the two neighboring nuclei. For this electron, since its position is fixed, there is no collapse and therefore no need for any constraint. We only need to constrain the two outermost electrons (see insert of Fig. 5) via Eq. (13) in the form

\[ -\frac{1}{r_2} - \frac{1}{r_3} = \Phi_s(r_1, R) + \Phi_t(r_1, 2R), \quad \text{Eq. (14)} \]

where \( r_i \) are defined in the insert of Fig. 5. For the linear \( \text{H}_3 \) ground state, adjacent electrons in the molecule have opposite spins, requiring the singlet potential \( \Phi_s(r_1, R) \). (We use the HM singlet potential given by Eq. (11)). In this case, the spins of the two outermost electrons must be parallel requiring the triplet potential \( \Phi_t(r_1, 2R) \). Minimizing the resulting energy function

\[ E = \frac{1}{r_1} + \frac{1}{2r_1^2} + V \quad \text{Eq. (15)} \]

yields the solid line potential energy curve of Fig. 5 which essentially goes through the “exact” solid circle results.
FIG. 5: Electron configuration and the ground state $E(R)$ of the linear $H_3$ molecule obtained from the constrained Bohr model (solid curve) and “exact” numerical solution of the Schrödinger equation (solid circles).

FIG. 6: Electron configuration and the ground state $E(R)$ of the triangular $H_3$ molecule. Solid curve is the result of the constrained Bohr model while solid circles are the “exact” numerical answer.

Insert of Fig. 6 shows the electrons’ positions for the equilateral triangle nuclei configuration. We assume that electron 1 has spin opposite to those of electrons 2 and 3. Symmetry dictates that electron 1 lies above, while electrons 2 and 3 lie below the nuclear plane along the bisector of the equilateral triangle. For electron 1 the constraint Eq. (13) reads

$$\frac{1}{r_2} = \Phi_s(r_1, R),$$

(16)

while for electrons 2 and 3 we have

$$\frac{2}{r_4} = \Phi_s(r_3, R) + \Phi_t(r_3, R).$$

(17)

Minimization of the energy function

$$E = \frac{1}{2r_1^2} + \frac{1}{r_3^2} + V$$

(18)

with the constraints (16) and (17) results in the solid line potential energy curve as shown in Fig. 6. Again for $\Phi_s$ we take the HM effective potential given by Eq. (11).

As in the case of the linear $H_3$ molecule, the constrained Bohr model yielded very accurate $E(R)$ over the entire range of internuclear separation. The constrained Bohr model also gives good results for other molecules, e.g., $Be_2$ as shown in Fig. 7 and $H_4$.

In the vicinity of the energy minimum the constrained Bohr model for $Be_2$ provides accuracy of a few milli Hartree with no fitting parameters. However, since $Be_2$ is very weakly bound the binding energy is off by about 50%. Nevertheles, the bond length remains quite accurate.

FIG. 7: Configuration of outer electrons and the ground state $E(R)$ of the $Be_2$ molecule obtained in the constrained Bohr model (solid curve) and the “exact” result (solid circles). The Bohr model provides accuracy of 0.003 Hartree.

In summary, we have shown that the atomic Bohr model, when supplemented by potential constraints obtained from quantum mechanics incorporating Pauli’s exclusion principle, gives a remarkably accurate description of diatomic and triatomic molecules. This constrained
Bohr model provides a physically appealing geometric picture of how multi-electron bonds are formed and holds promise for future applications to complex many-electron systems. Possible application of the model includes the simulation of biological molecules, where there is no ab initio way of doing the calculations with any other methods. The model can also be applied to the calculation of potential curves of molecules in a super strong magnetic field on surfaces of white dwarf and neutron stars.

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