Investigation of LCAO approximation for diatomic molecules in Hartree-Fock method

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Abstract
It was shown that the use of the conventional two-center LCAO approximation in the Hartree-Fock method results in non-equivalent description of the asymptotic properties of the total molecular wave function and MO’s in the directions of the united and separated atoms. This leads to a deviation of the Hartree-Fock potential curve calculated with using this approximation from that one obtained without it and which is growing with decreasing the internuclear separation. Additionally, the method has been developed for an investigation of the quality of the asymptotic behavior of the potential curves by analyzing their analytical properties. The direct comparison of the Hartree-Fock potential curves of CH and OH molecules obtained with and without LCAO approximation, as well an application of the proposed method for investigation of the analytical properties of them, display this shortcoming of the conventional two-center LCAO approximation.

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I. Introduction
Investigation of the asymptotic properties of the total molecular wave function and molecular orbitals is an efficient way to understand the physics of Coulomb interaction in molecules. In the first investigations published by Hund [1-3], Mulliken [4,5], Wigner and Witmer [6] the asymptotic or correlation properties of the total molecular wave functions and molecular orbitals (MO) of diatomic molecules with respect to changes the internuclear separation in the limits of the united and the separated atoms have been established and were presented qualitatively by Hund [1,2] and Mulliken [4,5] in the form of correlation diagrams. Later numerical solutions of the Hartree-Fock equation lead to construction of the numerical correlation diagrams for MO’s in some molecules and their ions [7-10].

Correlation of the total molecular wave function and MO’s in molecular orbital theory with the wave function and atomic orbitals (AO) of the united atom as well with the wave functions and MO’s of the separated atoms points that these asymptotic limits are equally described. On the other hand, the linear combination of atomic orbitals (LCAO) approximation, introduced by Lennard-Jones [11,12] and Mulliken [13], for an approximation of MOs in the Hartree-Fock equation [14-16] is based on the use of only the AO’s of the separated atoms. This means that the present treatment of the LCAO given by Roothaan [17]

\[ \varphi_i = \sum_{ij} c_{ij} \chi_j \],

where \( \varphi_i \) is i-MO, which represents by a set of AO \( \chi_j \), can equally well describe both asymptotic limits when the full set of AO \( \chi_j \) in three-dimensional space is used. However, in practice only finite set of AO’s of
separated atoms is used in (1). In this case, representation (1) cannot equally well describe both asymptotic limits.

In this connection, a new form of LCAO approximation in molecular orbital theory has been introduced in Refs. [18,19]. It is based on an assumption that any approximation used for a solution of the Hartree-Fock equation must equally describes the fundamental asymptotic properties of MO’s in the limits of the united and the separated atoms. This leads to the three-center LCAO approximation instead of the conventional two-center LCAO approximation.

For this reason, the asymptotic properties of the total molecular wave function obtained with LCAO approximation at Hartree-Fock method have been investigated in the present study. The main goal of the present investigation consists in demonstration that the use of the conventional two-center LCAO approximation in the Hartree-Fock method leads to a deviation of the diatomic potential curve calculated with it from that one obtained without it and which is increasing in the direction of the united atom. By other words, that the conventional two-center LCAO approximation leads to non-equivalent description of the asymptotic correlation properties of the total molecular wave function and MO’s in the directions of the united and the separated atoms. To show the importance of the third additional center (united atom) in quantum mechanical calculations of diatomic molecules a method for investigation of potential curves of diatomic molecules has been developed and applied for an investigation of the potential energy curves of CH and OH molecules calculated with conventional two-center LCAO approximation by Hartree-Fock method.

Obtained results are presented in the following order. Asymptotic properties of the Hamiltonian and the total wave function of the diatomic molecule are described in Sect. II. A derivation of the three-center LCAO approximation is outlined in Sect. III. A method for investigation of LCAO approximation in diatomic molecules is presented in Sect. IV. The investigation of potential curves of CH and OH molecules is given in Sect. V and conclusions are formulated in Sect. VI.

II. Diatomic Molecule as a Three-Center Quantum Mechanical Problem

Let us consider diatomic molecular Hamiltonian in the Born-Oppenheimer [20] approximation

$$H(R) = - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_i \left( \frac{Z_A}{|\vec{r}_i - \vec{R}_A|} + \frac{Z_B}{|\vec{r}_i - \vec{R}_B|} \right) + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|} + \frac{Z_A Z_B}{R}$$

(2),

where $Z_A$ and $Z_B$ are charges of nuclei $A$ and $B$, $N_A$ and $N_B$ are the number of electrons in atoms $A$ and $B$, $r_i$ is the vector of $i$-th electron, $R = |\vec{R}_A - \vec{R}_B|$ is the internuclear distance, and $\vec{R}_A$ and $\vec{R}_B$ are the vectors of nuclei $A$ and $B$.

A parametric dependence of $H(R)$ on $R$ gives us a possibility to investigate the correlation of a total molecular wave function with corresponding total atomic wave functions at the limits of the united atom at $R \to 0$ and the separated atoms at $R \to +\infty$. Thus, follow to Hund [1-3], Mulliken [4,5], Wigner and Witmer [6] we can obtain that at $R = 0$ molecular Hamiltonian (2) reduces to the Hamiltonian of a united atom

$$H(R) = - \sum_i \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_i \frac{Z_i}{|\vec{r}_i - \vec{R}|} + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

while the total molecular wave function transforms to the total atomic wave function of the united atom.

The limit $R = +\infty$ must be considered separately for homonuclear and heteronuclear molecules due to large difference between them connected with the absence of a permutational symmetry between atoms in heteronuclear molecules. For homonuclear molecules Hamiltonian (2) can be only split into a sum of two Hamiltonians of separated neutral atoms

$$H(R) = - \sum_{i=1}^N \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_{i=1}^N \frac{Z}{|\vec{r}_i - \vec{R}|} + \sum_{i<j} \frac{1}{|\vec{r}_i - \vec{r}_j|}$$

where $Z$ is the charge of the nuclear, $N$ is the number of electrons, and $R$ is the radius-vector of the nuclear.
In heteronuclear molecules the absence of a permutational symmetry between the atoms results in a transfer
of an electron charge between the atoms. Therefore, the state of an atom in a heteronuclear molecule corresponds
to an intermediate state, which is a state between a state of a neutral atom and a state of its cation or anion. For
this reason, at \( R \rightarrow +\infty \) the correlation of the total molecular wave function with the total wave functions of the
separated cations and anions can be observed along with the correlation with the total wave functions of the
separated neutral atoms. In this connection, at \( R = +\infty \) the molecular Hamiltonian (2) can be split into a sum of
two Hamiltonians of separated neutral atoms as well as into a sum of Hamiltonians of the cation

\[
H(R) = - \sum_{i}^{N_A-1} \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_{i}^{N_A-1} \frac{Z}{|r_i - R_A|} + \sum_{i<j}^{N_A-1} \frac{1}{|r_i - r_j|}
\]

and the anion

\[
H(R) = - \sum_{i}^{N_B+1} \frac{\hbar^2}{2m_i} \nabla_i^2 - \sum_{i}^{N_B+1} \frac{Z}{|r_i - R_B|} + \sum_{i<j}^{N_B+1} \frac{1}{|r_i - r_j|}
\]

of the separated atoms. Correspondingly, at \( R = +\infty \) the total molecular wave function can be expanded equally
into a sum of the total atomic wave functions of the separated neutral atoms or into a sum of the total atomic
wave functions of the cation and anion of these atoms.

Thus, the parametric dependence of the molecular Hamiltonian (2) on \( R \) results in a correlation of the ground
state molecular wave function with the total wave functions of the united atom and the two ground state wave
functions of the separated atoms in a homonuclear diatomic molecule. In the case of a heteronuclear diatomic
molecule additional correlation can appear with the two ground state wave functions of the cation and of the
anion. Hence, according to the superposition principle the total molecular wave function \( \psi \) of a homonuclear
diatomic molecule can be presented as the linear combination of tree wave functions

\[
\psi = c_A \psi_A + c_B \psi_B + c_U \psi_U
\]

where \( \psi_A \), \( \psi_B \) are the total wave functions of the separated neutral atoms and \( \psi_U \) is the total wave function of the
united atom. Similar to this a total wave function of a heteronuclear diatomic molecule can be presented as the
linear combination of five wave functions

\[
\psi = c_n \psi^n_A + c_{cat} \psi^{cat}_A + c_n \psi^n_B + c_{an} \psi^{an}_B + c_U \psi_U
\]

where indices \( n \), \( cat \), and \( an \) are used for a neutral atom, a cation, and an anion, respectively. In expressions (3)
and (4) each wave function \( \psi_A \), \( \psi_B \), and \( \psi_U \) connects with one of the three centers. Thus, the superposition principle
of quantum mechanics leads to a conclusion that the quantum mechanical problem for a diatomic
to a three-center problem with the corresponding multiconfiguration three-center representation of the
total molecular wave function.

### III. LCAO Approximation for Heteronuclear Diatomic Molecules in Molecular Orbital Theory

The Hartree-Fock equations [14-16] for Hamiltonians considered above can be derived for determination of
appropriate MO’s. The continuous dependence of molecular Hamiltonian (2) on \( R \) results in a correlation of the
Hartree-Fock MO’s with the corresponding AO’s of the limiting Hamiltonians. Therefore, the correlation properties
of the total molecular wave function and MO’s in the Hartree-Fock method are naturally preserved due
to the explicit dependence of molecular Hamiltonian (2) on \( R \).

The use of the LCAO approximation for a presentation of MO’s in the Hartree-Fock method significantly
simplifies the Hartree-Fock equation. The requirement that correct LCAO approximation has to be equally well
describes the asymptotic properties of MO’s in the limits of the united and the separated atoms leads to a
construction of the modified LCAO approximation described in Refs. [18,19]. It is clear, that this requirement
can only be fulfilled when all AO’s of the united and the separated atoms and AO’s of their cation and anion that
follows from the corresponding MO’s will be included in the general representation of MO \( \phi_i \) in LCAO
approximation given by expansion (1). The asymptotic correlation properties of MO’s at \( R = +\infty \) can explicitly
be fulfilled in LCAO approximation when AO’s of the separated atoms and AO’s of their cation and anion are
placed on the nuclei of appropriate atoms. The asymptotic properties of MO’s at \( R = 0 \) in LCAO approximation
However, calculations of the Hartree-Fock potential curves without LCAO approximation often are not easy available, then direct comparison of them will display this problem. Potential curves calculated with using conventional two-center LCAO approximation and without it are calculated without using such approximation will increase with decreases internuclear distance. When two Hartree-Fock potential curve obtained with the conventional two-center LCAO approximation from that one the shortcomings of LCAO approximation can be displayed by investigating the analytical properties of potential problem. In the case when only Hartree-Fock potential curves obtained with LCAO approximation are available, the approximation becomes worse with reduction of the internuclear separation. Therefore, deviations of the wave function in the direction of the united and separated atoms. For this reason, the quality of this approximation then a potential curve calculated with using this approximation will deviate from an analytical function in the limits of the united and the separated atoms. For effective description of the polarization of an atomic electron density in molecules other type of the off-center functions placed near the nucleus can be applied. An example of using such functions in the Hartree-Fock calculations of the H2 molecule at the limit of the complete set of basis functions is given in Ref. [19].

IV. A Method for Investigation of Diatomic Potential Energy Curves

The above consideration shows that the use of the conventional two-center LCAO approximation in the Hartree-Fock method results in non-equivalent description of the asymptotic properties of MO’s and the total molecular wave function in the direction of the united and separated atoms. For this reason, the quality of this approximation becomes worse with reduction of the internuclear separation. Therefore, deviations of the Hartree-Fock potential curve obtained with the conventional two-center LCAO approximation from that one calculated without using such approximation will increase with decreases internuclear distance. When two potential curves calculated with using conventional two-center LCAO approximation and without it are available, then direct comparison of them will display this problem.

However, calculations of the Hartree-Fock potential curves without LCAO approximation often are not easy problem. In the case when only Hartree-Fock potential curves obtained with LCAO approximation are available, the shortcomings of LCAO approximation can be displayed by investigating the analytical properties of potential curves of diatomic molecules. Usually potential curve diatomic molecule presents by infinite Dunham’s set, which mathematically is a Taylor set [24]. This means that the potential curve of a diatomic molecule is an analytical function. Thus, one can conclude that the behavior of a potential curve near a point of minimum is determined by the values of its derivatives in this point.

This analytical property of a potential curve permits to inspect the quality of LCAO approximation in dependence on the internuclear separation. If an employed LCAO approximation gives non-uniform approximation then a potential curve calculated with using this approximation will deviate from an analytical function in a vicinity of the point of minimum. This deviation can be visualized by comparing the original potential curve with the same curve restored from its derivatives at the point of minimum. Thus, we get a method to exam the quality of an employed LCAO approximation.

The method for an investigation of the quality of LCAO approximation by analyzing the analytical property of a diatomic potential curve can be presented as follows:

i) approximate an original potential curve, presented in a tabular form, by a polynomial;

ii) determine a point of minimum and calculate all possible derivatives of the potential curve at this point;
iii) calculate all possible Dunham coefficients and vibrational energy levels;
iv) determine turning points for the vibrational energy levels;
v) approximate the turning points (restored potential curve) by a polynomial;
vi) compare the initial potential curve with the restored one by constructing a graph of difference
between the potential curves in dependence on the deviation of the internuclear distance from
the minimum point of the potential curves.

When a potential curve is an analytical function, then an application of this protocol will give a straight or near
straight line along the abscissa axis. Otherwise, deviations from a straight line will be observed. These deviations
will show a quality of the employed LCAO approximation and will display the internuclear distances where
employed LCAO approximation is not correct.

The method for investigation of the analytical properties of potential curves presented above is a composite
method consisting of a few height precision numerical algorithms. The first three steps i), ii), and iii) are formed
the Dunham method for solving the vibrational Schrödinger equation with a potential curve presented in the
tabular form. The numerical algorithm of this method together with the rules for a tabulation of a potential curve
has been proposed in Refs. [25-29]. The turning points of vibrational energy levels can be calculated by a
method described in Ref. [30]. The asymptotic sets in this method were summed similar to those ones of the
Dunham method [25,26,29]. The computed turning points of vibration energy levels constitute the potential
curve restored from the derivatives of an original potential curve calculated at the point of minimum. The quasi-
Hermitian method developed for the approximation of potential curve points by an optimal polynomial in the
Dunham method [25,29] has been used to approximate these turning points. The optimum approximating
polynomials of the original potential curve and of the restored one permit to compare these potential curves and
to construct a graph of differences between values of these potential curves as a function of the deviation of the
internuclear distance from the minimum point.

V. The influence of the conventional LCAO approximation on the Hartree-Fock potential curves of the
CH and OH molecules

Potential curves of the ground states of CH and OH molecules have been calculated by the finite-difference
Hartree-Fock method [31] and the Hartree-Fock method with using conventional two-center LCAO
approximation [32]. These four potential curves were analyzed and compared as described above. The
investigations of the analytical properties of the potential curves of CH and OH molecules are presented on
Figure 1 and Figure 2, correspondingly. They show that the potential curves calculated with using conventional
two-center LCAO approximation display significantly large deviation from the analytical behavior in
comparison with the potential curves obtained by the finite-difference Hartree-Fock method. Besides that, the
potential curves calculated by the Hartree-Fock method with conventional two-centered LCAO approximation
display much large deviation from the analytical behavior in the direction of the united atom in comparison to
the direction of the separated atoms.
Figure 1. Investigation of the Hartree-Fock potential curves of the CH ($X^2\Pi$) molecule calculated with a conventional LCAO approximation and by a finite-difference method. Deviation of the potential curves (in a.u.) from an analytical behavior near the point of minimum.

The potential curves of CH and OH molecules can be directly compared. For this purpose, the graphs of differences between the potential curves obtained by the Hartree-Fock method with the conventional two-center LCAO approximation and those one’s obtained by the finite-difference Hartree-Fock method have been created. These graphs for the CH and OH molecules are presented on Figure 3 and Figure 4, correspondingly. These figures show that the deviations of the Hartree-Fock potential curves, calculated with the use of the conventional two-center LCAO approximation, from the potential curves, calculated by the finite-difference method, increase in the direction of a united atom.
Figure 2. Investigation of the Hartree-Fock potential curves of the OH ($X^2\Pi$) molecule calculated with a conventional LCAO approximation and by a finite-difference method. Deviation of the potential curves from an analytical behavior near the point of minimum.

Figure 3. Comparison of the Hartree-Fock potential curves of the CH ($X^2\Pi$) molecule. Deviation of the potential curve (in a.u.) obtained with the conventional two-center LCAO approximation from the potential curve obtained by the finite-difference method.
Figure 4. Comparison of the Hartree-Fock potential curves of the OH (X^2Π) molecule. Deviation of the potential curve (in a.u.) obtained with the conventional two-center LCAO approximation from the potential curve obtained be the finite-difference method.

Thus, the investigation of analytical properties of the potential curves of CH and OH molecules calculated by the finite-difference Hartree-Fock method and the Hartree-Fock method with using conventional two-center LCAO approximation and the direct comparison of these potential curves results in similar conclusion. The deviations of the Hartree-Fock potential curves obtained with conventional two-center LCAO approximation from the Hartree-Fock potential curves increase in the direction of the united atoms. Similar conclusion is also valid for the MO’s and the total molecular Hartree-Fock wave functions. Therefore, the use of the conventional two-center LCAO approximation in Hartree-Fock method results in non-equivalent description of the asymptotic properties of MO’s and the total molecular wave function in the directions of the united and separated atoms.

VI. Conclusions
The present investigation of the conventional two-center LCAO approximation in Hartree-Fock method shows that its application results in non-equivalent description of the asymptotic properties of the MO’s and the total molecular wave functions in the directions of the united and the separated atoms. This leads to the systematic deviation of the potential curve calculated with such LCAO approximation from the Hartree-Fock potential curve, which raises with decreasing internuclear separation, that is in the direction of the united atom.

On the other hand, tree-center LCAO approximation (5), presented above, is free from this shortcoming. The equivalent description of the asymptotic properties of the molecular wave function with this approximation permits significantly improve the best Hartree-Fock total energy of the H2 molecule which equals now to -1.133629571456 \text{E}\textsubscript{H} [19] in comparison with previous best value equals to –1.133629366 \text{E}\textsubscript{H} [33]. This also remove a gap between the best total Hartree-Fock energy obtained with LCAO approximation and that one equals to –1.13362957135 \text{E}\textsubscript{H} [34] calculated by the finite-difference method.

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