Non-adiabatic molecular Hamiltonian.

Canonical transformation coupling electronic
and vibrational motions.

Ivan Hubač a,b,c, Peter Babinec a,b, Martin Polášek c, Ján Urban b,
Pavel Mach b, Jozef Mášik b and Jerzy Leszczyński a

a Department of Chemistry, Jackson State University, 1400 Lynch Street,
P.O. Box 17910, Jackson, MS 39217, USA
b Division of Chemical Physics, Faculty of Mathematics and Physics, Comenius University,
Mlynská dolina F1, 842 15 Bratislava, Slovakia
c Institute of Physics, Faculty of Science, Silesian University, Bezručovo nám. 13,
746 01 Opava, Czech Republic

Abstract

The coupling of electronic and vibrational motion is studied by two canonical transformations namely normal coordinate transformation and momentum transformation on molecular Hamiltonian. It is shown that by these transformations we can pass from crude approximation to adiabatic approximation and then to non-adiabatic (diabatic) Hamiltonian. This leads to renormalized fermions and renormalized diabatic phonons. Simple calculations on $H_2$, $HD$, and $D_2$ systems are performed and compared with previous approaches. Problem of electronic quasi-degeneracy is discussed.

*Permanent and correspondence address


I. INTRODUCTION

Many atomic systems (e.g. molecules and/or crystals) are systems with interacting
electrons and nuclei and can be thus described by Schrödinger equation

\[ H\Psi = E\Psi \] (1)

In general case the number of degrees of freedom of such systems with coulomb interaction is
too large and even using high-performance computers to solve this equation becomes impossible. Therefore the only possibility to solve eq. (1) is to suggest some approximations [1–6]. The most important approximation and also most often used is the Born-Oppenheimer (BO) [7] and the adiabatic approximation. This approximation is based on the fact that masses
of nuclei are 1870 times heavier than the masses of electrons. This leads to the idea of
potential energy surface. Beside the many attempts to go beyond the BO approximation and
many different approaches certain facts are not clear completely. In this paper we decided
to study the coupling of electronic and vibrational motions by two canonical transforma-
tions namely normal coordinate and momentum transformations. Our approach is similar
to quasiparticle transformations often done in solid state physics. In order to make our
approach more transparent we repeat here main features of adiabatic approximation. We
follow the arguments of recent Kutzelnigg’s paper [8].

Let us write the total molecular Hamiltonian as

\[ H = T_N(R) + E_{NN}(R) + H_{EN}(r, R) + H_{EE}(r) \] (2)

where \( T_N(R) \) is the kinetic energy of nuclei, \( E_{NN}(R) \) is the interaction between nuclei, \( R \)
denotes nuclear coordinates, \( r \) denotes electronic coordinates, and \( H_{EN}(r, R) + H_{EE}(r) \) is
the electronic Hamiltonian

\[ H_{EN}(r, R) + H_{EE}(r) = T_E(r) + U_{EN}(r, R) + H_{EE}(r) \] (3)

where \( T_E(r) \) is the kinetic energy of electrons, \( U_{EN}(r, R) \) is the electron–nuclei interaction
term and \( H_{EE}(r) \) represents the electron-electron interaction. In Born and Huang [1–3]
approach the total wavefunction depending on the nuclear coordinates $R$ and the electronic coordinates $r$ is expanded as

$$\Psi(r, R) = \sum_k \psi_k(r, R) \chi_k(R),$$

where $\psi_k$ are a complete set of known functions of $r$ that depend parametrically on the nuclear coordinates $R$ and where the $\chi_k(R)$ are regarded as unknown. The $\psi_k$ are conventionally chosen as a set of eigenfunctions of the clamped nuclei (CN) Hamiltonian, but this is not necessarily a good choice, since this is usually not complete (without, the corresponding continuum functions, which one cannot include anyway). Both the BO and adiabatic approximation can be based on choosing a single term in eq. (4)

$$\Psi(r, R) = \psi_k(r, R) \chi_k(R),$$

This is referred as BO ansatz. This ansatz is taken as a variational trial function. Terms beyond the leading order in $m/M$ are neglected ( $m$ is the electronic and $M$ is nuclear mass, respectively). The problem with expansion (4) is that functions $\psi(r, R)$ contain except bound states also continuum function since it includes the centre of mass (COM) motion. Variation principle does not apply to continuum states. To avoid this problem we can separate COM motion. The remaining Hamiltonian for the relative motion of nuclei and electrons has then bound state solution. But there is a problem, because this separation mixes electronic with vibrational coordinates and also there is a question how to define molecule-fixed coordinate system. This is in detail discussed by Sutcliffe [3]. In the recent paper by Kutzelnigg [8] this problem is also discussed and it is shown how to derive in a rigorous manner adiabatic corrections using so called Born–Handy ansatz. There are few important steps to arrive at formula for a diabatic corrections. Firstly, one separates off COM motion. Secondly, (very important step) one does not specify the relative coordinates (which are to some extent arbitrary). In this way one arrives at relative Hamiltonian $H_{rel}$ [8] with trial wavefunction $\Psi_{rel}$. If we make BO ansatz

$$\Psi_{rel} = \psi(\cdots \rho_{ik}, \cdots \rho_{\mu\nu}, \cdots) \chi(\cdots \rho_{\mu\nu}, \cdots)$$

3
where \( \rho_{lk}, \rho_{\mu\nu} \) are non-specified relative coordinates and \( \psi \) is chosen as a solution of the CN Schrödinger equation. The adiabatic correction \( \Delta E \) take very simple form

\[
\Delta E = -\frac{1}{2} <\Psi| \sum_{\mu} M_\mu \nabla^2_\mu |\Psi>
\]

(7)

This formula was used by Handy [10]. It was used previously also by Sellers and Pulay [11]. (See also Davidov [9] for derivation). For practical calculation the identity

\[
\int \psi \frac{\partial^2}{\partial Q_i^2} \psi \ dr_i = -\int \left( \frac{\partial \psi}{\partial Q_i} \right)^2 \ dr_i
\]

(8)
can be used.

Note that practically in any textbook [9] the validity of BO approximation is justified only when

\[
\frac{\hbar \omega}{|E_n - E_m|} \ll 1
\]

(9)

when \( \omega \) is the frequency of harmonic vibrations arround the point \( R_0 \).

The aim of this paper is twofold:

i, We show how starting with molecular Hamiltonian (2) in crude adiabatic representation we arrive at adiabatic Hamiltonian by performing canonical transformations which mix together the electronic and vibrational motions (through normal coordinates). We derive simple formulae for adiabatic corrections, similar to eq. (7).

ii, We generalize canonical transformations (through momenta) arriving at non–adiabatic Hamiltonian. We introduce the idea of quasiparticles (renormalized electrons) and present the formulae how to obtain the "orbital energies", "correlation corrections" and non–adiabatic frequencies for these quasiparticles. Finally, we perform some simple model calculations to demonstrate how the method works.

II. THEORY

Let us start with electronic Hamiltonian (3) which we denote
\[ H_{EN}(r, R) + H_{EE}(r) = h + \nu^0, \]  

(10)

where \( h \) is the one-electron part representing the kinetic energy of the electrons and electron-nuclear attraction term, and \( \nu^0 \) is the two-electron part of the Hamiltonian corresponding to electron-electron repulsion term. For the purpose of diagrammatic many-body perturbation theory it will be efficient to work in second quantization formalism. The electronic Hamiltonian (10) has the form

\[
H_{EN} + H_{EE} = \sum_{PQ} <P|h|Q > a_p^\dagger a_Q \\
+ \frac{1}{2} \sum_{PQRS} <PQ|v^0|RS > a_{pQ}^\dagger a_s a_R
\]

(11)

where \( a_p^\dagger(a_Q) \) is the creation (annihilation) operator for electrons in the spinorbital basis \(|P>, |Q>, \cdots\). If we apply the Wick theorem to (11) we can write this equation as

\[
H_{EN} + H_{EE} = \sum_I h_{II} + \frac{1}{2} \sum_{IJ} \left( v^0_{IJJ} - v^0_{IJJI} \right) + \\
+ \sum_{PQ} h_{PQ}N \left[ a_{pQ}^\dagger a_Q \right] + \sum_{PQI} \left( v^0_{PIQI} - v^0_{PIIQ} \right) N \left[ a_{pQ}^\dagger a_Q \right] \\
+ \frac{1}{2} \sum_{PQRS} v^0_{PQRS}N \left[ a_{pQ}^\dagger a_s a_R \right]
\]

(12)

where \( v^0_{ABAB}(v^0_{ABBA}) \) denotes the coulomb (exchange) integral. One possibility is to work the within crude representation in which the spinorbital basis \(|P>, |Q>, \cdots\) is determined at some fixed (equilibrium coordinate \( R_o \)). Note that Hamiltonian (12) has \( 3N - 6 \) degrees of freedom (in fact 3N degrees of which 6 are zero). Hamiltonian (12) has only bound-state solutions. Let us divide individual terms of the Hamiltonian (12) into two parts. Namely calculated at point \( R_o \) and the terms which are shifted with respect to term at \( R_o \) (we use prime to denote these terms). The electronic Hamiltonian (12) can be rewritten as

\[
H_{EN} + H_{EE} = E_{SCF}^0 + h_{SCF}^\prime + \sum_P \varepsilon_P N \left[ a_p^\dagger a_P \right] \\
+ \sum_{PQ} h_{PQ}^\prime N \left[ a_p^\dagger a_Q \right]
\]
where \( E_{SCF}^{0} \) is the Hartree-Fock energy calculated at the point \( R_{0} \), and \( h_{SCF}' \) is the shift in the Hartree-Fock energy with respect to the point other than \( R_{0} \). The same is true for one-particle operator of (13), where \( \varepsilon_{P} \) are the one-particle Hartree-Fock energies calculated at point \( R_{0} \). The correlation operator is not changed because it does not depend on nuclear coordinates \( R \). For the notation see [12]. Let us perform the Taylor expansion for the energies \( E_{NN} \) and \( u_{SCF} \) around the point \( R_{0} \).

\[
E_{NN} = E_{NN}^{(0)} + E_{NN}' = \sum_{i=0}^{\infty} E_{NN}^{(i)}
\]

and

\[
u_{SCF} = u_{SCF}^{(0)} + u_{SCF}' = \sum_{i=0}^{\infty} u_{SCF}^{(i)}
\]

Using (14) and (15) we can rewrite our Hamiltonian (13) in the form

\[
H = E_{NN}^{(0)} + E_{SCF}^{(0)} + \sum_{r} \hbar \omega_{r} \left( b_{r}^{+} b_{r} + \frac{1}{2} \right) + u_{SCF}^{(2)} + \sum_{P} \varepsilon_{P} N \left[ a_{P}^{+} a_{P} \right] + \frac{1}{2} \sum_{PQRS} v_{PQRS}^{0} N \left[ a_{P}^{+} a_{Q}^{+} a_{S} a_{R} \right] + E_{NN}' - E_{NN}^{(2)} + u_{SCF}' - u_{SCF}^{(2)} + \sum_{PQ} u_{PQ} N \left[ a_{P}^{+} a_{Q} \right]
\]

where

\[
\sum_{r} \hbar \omega_{r} \left( b_{r}^{+} b_{r} + \frac{1}{2} \right) = T_{N} + E_{NN}^{(2)} + u_{SCF}^{(2)}
\]

\( \omega_{r} \) is the frequency of the harmonic oscillator and \( b^{+} (b) \) are boson (phonon) creation (annihilation) operators. In order to use the perturbation theory we have to split the Hamiltonian (16) onto the unperturbed part \( H_{0} \) and the perturbation \( H' \)

\[
H = H_{0} + H'
\]

Due to the crude approximation, we can partition the Hamiltonian (16) in the following way.

\[
\sum_{PQ} u_{PQ} N \left[ a_{P}^{+} a_{Q} \right]
\]
\[ H_0 = E_{NN}^{(0)} + E_{SCF}^{(0)} + \sum_p \varepsilon_p N \left[ a_p^+ a_p \right] + \sum_r \hbar \omega_r \left( b_r^+ b_r + \frac{1}{2} \right) \]  

(19)

and

\[ H' = H'_E + H'_F + H'_I. \]  

(20)

Where \( H' \) contains all the terms in (16) except (19). In eq. (16) all quantities were defined through the cartesian coordinates. For further purposes it will be natural to work in normal coordinates \( \{ B_r \} \). The normal coordinate in second quantized formalism is given as

\[ B_r = b_r + b_r^\dagger \]  

(21)

If we transform Hamiltonian (16) into normal coordinates we arrive at the following expressions [12]

\[ H = E_{NN}^{(0)} + E_{SCF}^{(0)} + \sum_p \varepsilon_p N \left[ a_p^+ a_p \right] + \sum_r \hbar \omega_r \left( b_r^+ b_r + \frac{1}{2} \right) \]

\[ + \frac{1}{2} \sum_{PQRS} v_{PQRS}^0 \left[ a_P^+ a_Q^+ a_S a_R \right] \{ \equiv H'_E \} \]

\[ + \sum_{n=1}^{\infty} \left( \varepsilon_{N}^{(k,n-2k)} + \varepsilon_{SCF}^{(k,n-2k)} \right) \cdot B^{n-2k} \{ \equiv H'_F \} \]

\[ + \sum_{n=1}^{\infty} \sum_{k=0}^{[n/2]} \sum_{PQ} u_{PQ}^{(k,n-2k)} \cdot B^{n-2k} N[a_P^+ a_Q] \{ \equiv H'_I \} \]  

(22)

The term \( H'_E \) is the electron correlation operator, the term \( H'_F \) corresponds to phonon-phonon interaction and \( H'_I \) corresponds to electron-phonon interaction. If we analyze the last term \( H'_I \) we see that when using crude approximation this corresponds to such phonons that force constant in eq. (17) is given as a second derivative of electron–nuclei interaction with respect to normal coordinates. Because we used crude adiabatic approximation in which minimum of the energy is at the point \( R_o \), this is also reflected by basis set used. Therefore this approximation does not properly describes the physical vibrations i.e. if we move the nuclei, electrons are distributed according to the minimum of energy at point \( R_o \) and they do not feel correspondingly the \( R \) dependence. The perturbation term \( H'_I \) which corresponds
to electron–phonon interaction is too large and thus perturbation theory based on splitting
given by eq. (19, 20) will not converge [13]. Natural way to improve this situation will be to
use basis set which is generally $R$ dependent. We can do this in second–quantized formalism
in a way that we pass from electron creation (annihilation) operators $a^+_P (a_Q)$ which act on
$R_o$ dependent basis set to a new fermion creation (annihilation) operators $\tilde{a}^+_P (\tilde{a}_Q)$ which act
on $R$ dependent basis. Similar transformation was studied for solid state theory by Wagner [14], who also discuss the convergency properties of adiabatic approximation [15]. This we
can achieve by canonical transformation passing from old electron operators $a^+_P (a_Q)$ to new
operators $\tilde{a}^+_P (\tilde{a}_Q)$ through normal coordinates $B_r$. In this way we can pass from crude
adiabatic Hamiltonian to what is called clamped nucleus Hamiltonian and corresponding
clamped nucleus wavefunction $\Psi(r,R)$. The proof that this is a canonical transformation is in [12].

$$\tilde{a}_P = a_P + \sum Q \sum_{k=1}^{\infty} \frac{1}{k!} \sum_{r_1...r_k} C_{PQ}^{r_1...r_k} B_{r_1} \ldots B_{r_k} a_Q$$

$$\tilde{a}^+_P = a^+_P + \sum Q \sum_{k=1}^{\infty} \frac{1}{k!} \sum_{r_1...r_k} C_{PQ}^{r_1...r_k} B_{r_1} \ldots B_{r_k} a^+_Q,$$

where $B_r$ are second quantized normal coordinates. In short notation we can also write [12]

$$\tilde{a}_P = \sum Q \sum_{k=0}^{\infty} \frac{1}{k!} C_{PQ}^{(k)*} B^k a_Q$$

$$= \sum Q C_{PQ} a_Q$$

$$= \sum Q C_{PQ} a_Q$$

$$\tilde{a}^+_P = \sum Q \sum_{k=0}^{\infty} \frac{1}{k!} C_{PQ}^{(k)} a^+_Q$$

$$= \sum Q C_{PQ} a^+_Q$$

$$= \sum Q C_{PQ} a^+_Q$$

$$= \sum Q C_{PQ} a^+_Q$$
We also perform analogous canonical transformation for phonons

\[ \tilde{b}_r = b_r + \sum_{PQ} \sum_{k=0}^{\infty} \frac{1}{k!} \sum_{s_1 \ldots s_k} d_{sPQ}^{s_1 \ldots s_k} B_{s_1} \ldots B_{s_k} a_P^a a_Q^a, \]  

(27)

\[ \tilde{b}_r^+ = b_r^+ + \sum_{PQ} \sum_{k=0}^{\infty} \frac{1}{k!} \sum_{s_1 \ldots s_k} d_{sPQ}^{s_1 \ldots s_k^*} B_{s_1} \ldots B_{s_k} a_P^a a_Q^a, \]  

(28)

The coefficients \( C_{PQ} \) (\( C_{PQ}^+ \)) in eqs. (25, 26) are determined so that \( \tilde{a}_P (\tilde{a}_P^+) \) satisfy fermion anticommutation relation. The coefficients \( d_{rPQ} (\ d_{rPQ}^+ \) in eqs. (27, 28) are determined so that \( \tilde{b}_r (\tilde{b}_r^+) \) satisfy boson commutation relation. Finally we ask fermions \( \tilde{a}_P (\tilde{a}_P^+) \) to commute with bosons \( \tilde{b}_r (\tilde{b}_r^+) \). This means that we can write similarly as in (5) the total wave function \( \Psi(r, R) \) as a product of fermion wave function \( \psi_k(r, R) \) and boson wave function \( \chi_k \) as \( \Phi(r, R) \)

\[ \Phi(r, R) = \psi_k(r, R) \chi_k(R), \]  

(29)

It is easy to show that we have two invariants of transformations, namely number operator of fermions

\[ \tilde{N} = N. \]  

(30)

and normal coordinate

\[ \tilde{B} = B \]  

(31)

The next step is that we find inverse transformations to (25-28) and substitute these inverse transformations into eq. (22) and then applying Wick theorem, we requantize the whole Hamiltonian (19) in a new fermions and bosons [12]. This leads to new V-E Hamiltonian (we omit - on the second quantized operators)

\[ H = H_A + H_B \]  

(32)

where
\[ H_A = E_{NN}(B) - E_{NN}^{(2)}(B) - V_N^{(2)}(B) + \sum_{RSI} h_{RS}(B)C_{RI}C_{SI} \]

\[ + \frac{1}{2} \sum_{RSTUJ} (v_{RSTU}^0 - v_{RSTU}^0)C_{RI}C_{SI}C_{TJ}C_{UJ} \]

\[ + \sum_{PQRS} h_{RS}C_{RP}C_{SQ}N \left[ a_P^+a_Q \right] \]

\[ + \sum_{PQRSTU} (v_{RSTU}^0 - v_{RSTU}^0)C_{RP}C_{SQ}C_{TJ}C_{UJ}N \left[ a_P^+a_Q \right] \]

\[ + \sum_{PQRSTUVW} v_{TUVW}^0C_{TP}C_{UQ}C_{VR}C_{WS}N \left[ a_P^+a_Q^+a_Ra_S \right] \]

(33)

and

\[ H_B = \sum_r \hbar \omega_r \left( b_r^+b_r + \frac{1}{2} \right) \]

\[ + \sum_{PQR} \hbar \omega_r (b_r^+d_{rPQ} + d_{rQP}b_r) \frac{1}{2} \]

\[ + \sum_{Alr} \hbar \omega_r (d_{rAl})^2 + \sum_{PQA} \hbar \omega_r (d_{rPA}d_{rQA} - d_{rP1}d_{rQ1}) \frac{1}{2} \]

\[ + \sum_{PQRSr} \hbar \omega_r d_{rPS}d_{rQR}N \left[ a_P^+a_Q^+a_Ra_S \right] \]

(34)

If we introduce the following quantities

\[ E_{SCF} = \sum_{RSI} h_{RS}C_{RI}C_{SI} \]

\[ + \frac{1}{2} \sum_{RSTUJ} (v_{RSTU}^0 - v_{RSTU}^0)C_{RI}C_{SI}C_{TJ}C_{UJ} \]

(35)

the new Hartree-Fock operator \( f \) with the matrix elements

\[ f_{PQ} = \sum_{RS} h_{RS}C_{RP}C_{SQ} \]

\[ + \sum_{RSTU} (v_{RSTU}^0 - v_{RSTU}^0)C_{RP}C_{SQ}C_{TJ}C_{UJ} \]

(36)

and the new two-particle integral

\[ v_{PQRS} = \sum_{TUVW} v_{TUVW}^0C_{TP}C_{UQ}C_{VR}C_{WS} \]

(37)

We can rewrite our Hamiltonian \( H_A \) (33) to the form
\( H_A = E_{\text{NN}} - E_{\text{NN}}^{(2)} - V_N^{(2)} + E_{\text{SCF}} + \sum_{PQ} f_{PQ} N \left[ a_P^+ a_Q \right] \)
\( + \frac{1}{2} \sum_{PQRS} v_{PQRS} N \left[ a_P^+ a_Q^+ a_S a_R \right] \)

Here in eq. (38) \( \sum_{PQ} f_{PQ} N \left[ a_P^+ a_Q \right] \) is new Hartree-Fock operator for a new fermions (25), (26), operator \( \frac{1}{2} \sum_{PQRS} v_{PQRS} N \left[ a_P^+ a_Q^+ a_S a_R \right] \) is a new fermion correlation operator and \( E_{\text{SCF}} \) is a new fermion Hartree-Fock energy. Our new basis set is obtained by diagonalizing the operator \( f \) from eq. (36). The new Fermi vacuum is renormalized Fermi vacuum and new fermions are renormalized electrons. The diagonalization of \( f \) operator (36) leads to coupled perturbed Hartree-Fock (CPHF) equations [16–18]. Similarly operators \( \bar{b}_r \) and \( \bar{b}_r \) correspond to renormalized phonons. Using the quasiparticle canonical transformations (25 –28) and the Wick theorem the V-E Hamiltonian takes the form

\[ H = H_A + B_B \]  

where

\[ H_A = E_{\text{NN}}^0 + E_{\text{SCF}}^0 + \sum_p \epsilon_p N \left[ a_p^+ a_p \right] \]
\( + \sum_n \sum_{k=0}^{[n/2]} E^{(k,n-2k)} . B^{(n-2k)} \)
\( + \sum_n \sum_{k=0}^{[n/2]} \sum_{PQ} f^{(k,n-2k)}_{PQ} B^{(n-2k)} N \left[ a_P^+ a_Q \right] \)
\( + \frac{1}{2} \sum_n \sum_{k=0}^{[n/2]} \sum_{PQRS} v^{(k,n-2k)}_{PQRS} . B^{(n-2k)} N \left[ a_P^+ a_Q^+ a_S a_R \right] \).  

and

\[ H_B = \sum_r \hbar \omega_r \left( b_r^+ b_r + \frac{1}{2} \right) \]
\( + \sum_{AIr} \hbar \omega_r \left( d_{rAI} \right)^2 + \sum_{PQ} \hbar \omega_r \left( b_r^+ d_{rPQ} + d_{rQP} b_r \right) N \left[ a_P^+ a_Q \right] \)
\( + \sum_{PQA} \hbar \omega_r \left( d_{rPA} d_{rQA} - d_{rPA} d_{rQA} \right) N \left[ a_P^+ a_Q \right] \)
\( + \sum_{PQRS} \hbar \omega_r d_{rPS} d_{rQRS} N \left[ a_P^+ a_Q^+ a_S a_R \right] \).
As we have shown in [12,13] this quasiparticle transformation leads from crude adiabatic to adiabatic Hamiltonian. This Hamiltonian (39) is adiabatic Hamiltonian. Note that the force constant for harmonic oscillators is given as second derivative of $E_{SCF}$ at point $R_o$. We shall call the corresponding phonons as adiabatic phonons.

**III. DIABATIC CANONICAL TRANSFORMATION**

In previous part we developed canonical transformation (through normal coordinates) by which we were able to pass from crude adiabatic to adiabatic Hamiltonian. We started with crude adiabatic molecular Hamiltonian on which we applied canonical transformation on second quantized operators

$$\tilde{a}_P = \sum_Q C_{PQ}(B) a_Q$$

(42)

$$\tilde{a}_P^+ = \sum_Q C_{PQ}(B)^+ a_Q^+$$

(43)

$$\tilde{b} = b_r + \sum_{PQ} d_{rPQ}(B) a_P^+ a_Q$$

(44)

$$\tilde{b}_r = b_r^+ + \sum_{PQ} d_{rQ}^{+P}(B)^+ a_P^+ a_Q$$

(45)

where operators $\tilde{a}_P$ ($\tilde{a}_P^+$) corresponds to fermions and operators $\tilde{b}$ ($\tilde{b}_r^+$) to bosons and $B = b + b^+$ is the normal coordinate. The coefficients $C_{PQ}$ ($d_{rPQ}$) can be found from the solution of CPHF equations. We also found that adiabatic corrections can be calculated as perturbation corrections, which mean that we expect that adiabatic corrections represents small perturbation. The situation can be more complex if we cannot treat non-adiabaticity as a perturbation. This is the case when non-adiabaticity can cause strong coupling between two or more electronic states. In order to treat such situations we can procede in a way in which we generalize transformations (25)-(28). In these equations the expansion coefficients $C$ and $d$ were functions of normal coordinates $B = b + b^+$. 

12
The generalization can be done in a way that these coefficients are some general functions $C_{PQ}(b, b^+)$ and $d_{rPQ}(b, b^+)$ of $b$ and $b^+$ operators. We can expect that these coefficients will be not only the function of normal coordinate $B = b + b^+$ but also the function of momentum $\tilde{B} = b - b^+$. Therefore general transformations will have the form \[20,19\]

\[
\tilde{a}_P = \sum_Q C_{PQ}(B, \tilde{B}) a_Q \tag{46}
\]

\[
\tilde{a}_P^+ = \sum_Q C_{PQ}(B, \tilde{B})^+ a_Q^+ \tag{47}
\]

\[
\tilde{b} = b_r + \sum_{PQ} d_{rPQ}(B, \tilde{B}) a_P^+ a_Q \tag{48}
\]

\[
\tilde{b}_r = b_r^+ + \sum_{PQ} d_{rQP}(B, \tilde{B}) a_P^+ a_Q \tag{49}
\]

Such transformations would be rather complex, therefore we try simple approximation

\[C(B, \tilde{B}) = C(B) \tilde{C}(\tilde{B}) \tag{50}\]

Further we can proceed similarly as in the case of adiabatic approximation. We shall not present here the details. These are presented in \[20,19\]. We just mention the most important features of our transformation \[46-50\]. Firstly, when passing from crude adiabatic to adiabatic approximation the force constant changed from second derivative of electron–nuclei interaction $u^{(2)}_{SCF}$ to second derivative of Hatree–Fock energy $E^{(2)}_{SCF}$. Therefore when performing transformation \[46-50\] we expect change of force constant and therefore change of the vibrational part of Hamiltonian

\[H_B = E_{kin}(\tilde{B}) + E_{pot}(B) \tag{51}\]

The potential energy is determined by the quadratic part of the nuclear energy $E_{NN}^{2}(B)$ as well as by some potential energy $V_N^{(2)}(B)$ which is a quadratic function of coordinate operators and has its origin in the interaction of the electrons with the vibrating nuclei. Therefore we have
In the case of kinetic energy term this was identical with the kinetic energy of the nuclei in the case of adiabatic approximation. In the case of the breakdown of adiabatic approximation we have to remember the finite mass of electrons and therefore to introduce more general kinetic energy term. Therefore, we add to the kinetic energy of the nuclei \( T_N(B) \) some other yet unknown term which will be the quadratic function of momentum operator

\[
E_{\text{kin}}(\tilde{B}) = T_N(\tilde{B}) + W_N^r(\tilde{B})
\]  

The total vibrational–electronic Hamiltonian

\[
H = H_A + H_B
\]

will have the form

\[
H_B = T_N^r(\tilde{B}) + W_N^r(\tilde{B}) + E_{NN}(B) + V_N^r(B)
\]

and

\[
H_A = E_{NN}(B) - E_{NN}^r(B) - V_N^r(B) - W_N^r(\tilde{B})
\]

Secondly, coefficients \( C_{PQ} \) and \( \tilde{C}_{PQ} \) are determined through equations

\[
u_{PQ}^r + (\bar{\varepsilon}_P^0 - \bar{\varepsilon}_Q^0) C_{PQ}^r + \sum_{AI} \left[(V_{PQA}^0 - V_{PIAQ}^0) C_{AI}^r - (V_{PQAI}^0 - V_{PAIQ}^0) C_{IA}^r\right]

- \hbar \omega \tilde{C}_{PQ}^r = \bar{\varepsilon}_P^r \delta_{PQ}
\]

\[
(\bar{\varepsilon}_P^0 - \bar{\varepsilon}_Q^0) \tilde{C}_{PQ}^r + \sum_{AI} \left[(V_{PQA}^0 - V_{PIAQ}^0) \tilde{C}_{AI}^r - (V_{PQAI}^0 - V_{PAIQ}^0) \tilde{C}_{IA}^r\right]

- \hbar \omega \tilde{C}_{PQ}^r = \bar{\varepsilon}_P^r \delta_{PQ}
\]
where $\hbar \omega_r$ is the new non-adiabatic phonon given by

$$H_B = \sum_r \hbar \omega_r (b_r^+ b_r + \frac{1}{2})$$  \hspace{1cm} (59)

The expressions for extra terms $V_{N}^{(2)}(B)$ and $W_{N}^{(2)}(\tilde{B})$ in (55) are given as

$$V_{N}^{rs} = \sum_l u_{lI}^r + \sum_{iA} \left[ (u_{rAI}^s + \hbar \omega_r \tilde{C}_{rAI}^s) C_{sIA}^r + (u_{rAI}^r + \hbar \omega_s \tilde{C}_{rAI}^r) C_{sIA}^r \right]$$  \hspace{1cm} (60)

and

$$W_{N}^{rs} = 2\hbar \omega_r \sum_{AI} C_{AI}^r \tilde{C}_{sIA}^s$$  \hspace{1cm} (61)

This means that the resulting vibrational frequency $\omega$ depends explicitly on coefficients $\tilde{C}_{PQ}^r$ and $C_{PQ}^r$.

Finally fermion part of Hamiltonian will be given as

$$H_F = H_F^0 + H_F' + H_F'' + H_F'''$$  \hspace{1cm} (62)

For the ground state energy we get

$$H_F^0 = E_{NN}^0 + E_{SCF}^0 + \sum_{AIr} \hbar \omega_r (|C_{rA}^r|^2 - |\tilde{C}_{rAI}^r|^2)$$  \hspace{1cm} (63)

One-fermion part will be

$$H_{F'} = \sum_P \varepsilon_P^0 N[a_P^+ a_P] + \sum_{PQr} \hbar \omega_r \left[ \sum_A (C_{PA}^r C_{QA}^r - \tilde{C}_{PA}^r \tilde{C}_{QA}^r) - \sum_l (C_{P1}^r C_{Ql}^r - \tilde{C}_{P1}^r \tilde{C}_{Ql}^r) \right] N[a_P^+ a_Q] - 2 \sum_{PQr} E_{PQ}^r \tilde{C}_{PQ}^r N[a_P^+ a_Q]$$

$$+ \sum_{PQr} \left[ (h(P) - p(P))\varepsilon_P^r + (h(Q) - p(Q))\varepsilon_Q^r \right] \tilde{C}_{PQ}^r N[a_P^+ a_Q]$$

$$- \sum_{PQAIR} \left[ (v_{PQA}^r - v_{PQA}^0) \tilde{C}_{rIA}^r + \left(v_{PQA}^r - v_{PQA}^0\right) C_{rIA}^r \right] N[a_P^+ a_Q a_S a_R]$$  \hspace{1cm} (64)

Two-fermion part will be

$$H_{F''} = \frac{1}{2} \sum_{PQRS} v_{PQRS}^0 N[a_P^+ a_Q^+ a_S a_R]$$

15
The bosonic part of Hamiltonian $H$ form as in eq. (59) we can proceed as follows. Three-fermion part will be (as a result of transformation (50) the three fermion term appears)

\[ H_{F''} = -2 \sum_{PQRSTUVr} (v_{PQVT}^{0} C_{RS}^{p} - v_{PQST}^{0} C_{PV}^{p}) \tilde{C}_{UR}^{rs} N[a_{p}^{-} a_{Q}^{-} a_{S}^{-} a_{R}^{-}] \]

The bosonic part of Hamiltonian $H_{B}$ is not given in a diagonal form. To bring it to diagonal form as in eq. (59) we can proceed as follows.

\[
H_{B} = T_{N} + E_{NN}^{(2)} + \sum_{r,s} E_{SCF}^{rs} - \sum_{I} \left[ \epsilon_{I}^{r} S_{II}^{r} + \frac{1}{2} \left( \epsilon_{I}^{s} S_{II}^{s} + \epsilon_{I}^{r} S_{II}^{r} \right) \right] + \sum_{RI} \left[ (f_{RI} - \epsilon_{I}^{0} S_{RI}^{r} + \hbar \omega_{r} \tilde{C}_{RI}^{r}) \tilde{C}_{RI}^{s} \right]
+ \left( f_{RI} - \epsilon_{I}^{0} S_{RI}^{s} + \hbar \omega_{s} \tilde{C}_{RI}^{s} \right) \tilde{C}_{RI}^{r} B_{r} B_{s}
+ \sum_{AI} 2\hbar \omega_{r} \sum_{A} \left( \tilde{C}_{AI}^{r} + <A|I^{r}> \right) \tilde{C}_{AI}^{s} B_{r} B_{s} \]  

(67)

Our aim is to bring this Hamiltonian into diagonal form. We can extract adiabatic part ($\hbar \omega_{r}^{0}$) and we get

\[
H_{B} = \sum_{r} \hbar \omega_{r}^{0} (b_{r}^{+} b_{s} + \frac{1}{2}) \delta_{rs} + F_{rs}^{1} + F_{rs}^{2}
\]

(68)

where

\[
F_{rs}^{1} = 2 \sum_{r,s} \left( \sum_{R,I} \left[ (f_{RI}^{s} - \epsilon_{I}^{0} (\tilde{C}_{RI}^{r} - \tilde{C}_{RI}^{s}) + \hbar \omega_{r} \tilde{C}_{RI}^{r} \tilde{C}_{RI}^{s} \right) B_{r} B_{s} \right)
\]

(69)
\[
F_{rs}^2 = 2 \sum_{r,s} \hbar \omega_r \left\{ \sum_{AI} (\hat{C}_{AI}^r + < A | I' > \hat{C}_{AI}^s) \right\} \hat{B}_r \hat{B}_s
\]

(70)

where \( \hat{C}_{RI}^r \) is identical with \( \hat{C}_{RI}^r \) coefficients from adiabatic transformation eqs. (23, 24). If we substitute in eq. (69) and (70) for \( B_r = b_r^+ + b_r \) and \( \tilde{B}_r = b_r - b_r^+ \) we get for (68) the expression

\[
H_B = \sum_{rs} \left[ A_{rs} b_r^+ b_s + \frac{1}{2} B_{rs} (b_r^+ b_s^+ + b_r b_s) \right]
\]

(71)

where

\[
B_{rs} = 2(F_{rs}^1 + F_{rs}^2)
\]

(72)

\[
A_{rs} = F_{rs}^1 + F_{sr}^1 - F_{rs}^2 - F_{sr}^2
\]

(73)

Diagonalizing the above Hamiltonian we obtain diabatic frequencies

\[
H_B = \sum_r \hbar \omega_r^d (b_r^+ b_r + \frac{1}{2})
\]

(74)

Hamiltonian (71) has a form of quadratic Hamiltonian [21,22] and can be diagonalized by Bogoljubov transformation, which leads to the condition

\[
det \begin{pmatrix}
\hat{A} - \omega^d \hat{1} & \hat{B} \\
-\hat{B} & -\hat{A} - \omega^d \hat{1}
\end{pmatrix} = 0
\]

(75)

Secular equation (75) gives us diabatic phonons \( \hbar \omega_r^d \).

If we look at eq. (11) we see that we have corrections due to non–adiabaticity to one-particle part as well as to two-particle part. We see the hierarchical structure of our Hamiltonian. If the non–adiabatic coupling is small i.e. \( \tilde{C} \) goes to zero and we have adiabatic Hamiltonian. If this coupling is strong we cannot use adiabatic approximation but we have to work with full V-E Hamiltonian (54).
IV. CALCULATIONS

In order to compare our approach with other approaches dealing with adiabatic corrections we perform simple model calculations for adiabatic corrections to ground state energy. We start with adiabatic Hamiltonian (32). We now perform the following approximation. We limit ourselves to finite orders of Taylor expansion of the operators $H_A'$ and $H_B'$. We shall use similar approximation as in [23]. The diagrammatic representation of our approximate Hamiltonian will be

$$H = H_o + H' = E_{NN}^o + E_{SCF}^o \sum_P \epsilon_P N [a_P^+ a_P]$$

$$+ \sum_r \hbar \omega_r \left( b_r^+ b_r + \frac{1}{2} \right)$$

(76)

The adiabatic corrections to the ground state of $H_2, HD,$ and $D_2$ we shall calculate using second–order Rayleigh–Schrödinger many-body perturbation theory (RS–MBPT) and our Hamiltonian (76). If we assume that we know the solution of the unperturbed Schrödinger equation

18
\[ H_0 | \varphi_o > = E_o | \varphi_o > , \]  

(77)

where \( H_0 \) is the unperturbed Hamiltonian \( H_A^o + H_B^o \) where

\[ H_A^o = E_{NN}^o + E_{SCF}^o + \sum_P \epsilon_P N [a_P^+ a_P] \]  

(78)

and

\[ H_B^o = \sum_r \hbar \omega_r \left( b_r^+ b_r + \frac{1}{2} \right) \]  

(79)

The perturbed (exact) Schrödinger equation will read

\[ H | \Psi > = \mathcal{E} | \Psi > , \]  

(80)

where \( H \) will be our Hamiltonian (76). The perturbed energy \( \mathcal{E} \) will be given through the RS-MBPT expansion as

\[ \mathcal{E} = E_o + < \varphi_o | H' | \varphi_o > + < \varphi_o | H' Q_o H' | \varphi_o > + \ldots , \]  

(81)

where \( H' \) is the perturbation and \( Q_o \) is the resolvent

\[ Q_o = \sum_{i \neq 0} \frac{| \varphi_i > < \varphi_i |}{E_0 - E_i} \]  

(82)

Since our sets of boson creation and annihilation operators and fermion creation and annihilation operators commute we can write our unperturbed wavefunction \( | \varphi_o > \) as the product of the fermion state vector \( | \psi_o > \) and the boson state vector \( | \chi_o > \), i.e.

\[ | \varphi_o >= | \psi_o > | \chi_o > \]  

(83)

Further we want to study the nonadiabatic corrections to the ground state. Therefore \( | \psi_o > \) will be the unperturbed ground state wave function (we shall use Hartree–Fock ground state Slater determinant –Fermi vacuum) and \( | \chi_o > \) will be boson ground state –boson vacuum \( | 0 > \).

\[ | \chi_0 >= | 0 > . \]  

(84)
The exact ground state energy will be given by perturbation expansion (up to the second order)

\[ E = \langle \psi_0 | < 0 | H_0 | 0 > | \psi_0 > \]
\[ + \langle \psi_0 | < 0 | H' | 0 > | \psi_0 > \]
\[ + \langle \psi_0 | < 0 | H'Q_0H' | 0 > | \psi_0 > + ... \]

(85)

Substituting for \( H_o = H^a + H^b \) from (78, 79) into the first term in (85) we get

\[ \langle \psi_0 | < 0 | H_o | 0 > | \psi_0 > = E_{NN}^{o} + E_{SCF}^{o} + \sum_r \frac{1}{2} \hbar \omega_r \]

(86)

We shall not present all terms for perturbation corrections from the right hand side of eq. (85). There are corrections which corresponds to electron correlation, anharmonicity corrections and adiabatic corrections [23]. We shall pay attention only to adiabatic corrections given through second-order term in eq. (85). Analyzing diagrammatic contributions through the Hamiltonian (76) we find that the adiabatic corrections are given through the second up to fourth term in eq. (85). From these terms we calculate only contributions from the first and the second term which are given through the first order of Taylor expansion and these terms are used in second order RS–MBPT. We obtain the following simple expressions

\[ \langle \psi_0 | < 0 | H' | 0 > | \psi_0 > \sim \]
\[ \sum_{AIr} \hbar \omega_r \left( C^{r}_{AI} + < A(0) | I > \right)^2 \]
\[ + \sum_{AIr} \hbar^2 \omega^2_r \left( C^{r}_{AI} + < A(0) | I > \right)^2 \cdot (\varepsilon_I - \varepsilon_A - \hbar \omega_r)^{-1} \]
\[ + \sum_{AIr} \hbar^2 \omega^2_r \left( C^{r}_{AI} + < A(0) | I > \right)^2 \cdot (\varepsilon_I - \varepsilon_A + \hbar \omega_r)^{-1} \]
\[ \approx \sum_{AIr} \hbar \omega_r \left( C^{r}_{AI} + < A(0) | I > \right)^2 \]
\[ + 2 \sum_{AIr} \hbar^2 \omega^2_r \left( C^{r}_{AI} + < A(0) | I > \right)^2 \cdot (\varepsilon_I - \varepsilon_A)^{-1} \]

(87)
For the notation see \cite{20,23}. We believe these three terms on right hand side of \cite{87} represents the dominant contributions to adiabatic corrections. The last formula is valid due to the eq. \cite{9}. This formula was used to calculate the adiabatic corrections to the ground state energy of the \( H_2 \), \( D_2 \), and \( HD \) molecules. Results in \( cm^{-1} \) are presented in Table I. We see that the structure of this formula is similar to eq. \cite{7} except that we use RS–MBPT. We also used the same approach to calculate the adiabatic corrections to the energies of the first vibrational transitions for the same molecules \cite{23}. Analyzing eq. \cite{87} we can see that the first term on the right hand side of eq.\( (87) \) is always positive and correspond to largest contribution, while the second term on right hand side of eq. \cite{87} is always negative and represents smaller contribution than the previous term. Therefore we can expect that the eq. \cite{87} should converge to the true value of adiabatic correction from above. This also explain the larger values for \( H_2 \), \( D_2 \), and \( HD \) adiabatic correction obtained through eq. \cite{87} than true value obtained by Wolniewicz \cite{24}. Another source of difference can be basis set used and also the contribution from other terms in \cite{11}. In our calculation we have obtained for \( H_2 \) value of 136.89 \( cm^{-1} \) using Roos Augmented Triple Zeta ANO \cite{25} basis set. Handy \cite{10} using basis set of similar quality as used in our calculations obtained value 101 \( cm^{-1} \). Similar value of adiabatic correction was obtained also in an older study by Wolfsberg \cite{26}. Kutzelnigg \cite{27} in his paper using wave function expansion consisting 1200 functions obtained Wolniewicz \cite{24} value 114.591 \( cm^{-1} \). It is apparent that calculations of adiabatic corrections are strongly basis set dependent.

V. CONCLUSIONS

In this article we performed simple model calculations of adiabatic corrections for ground state energy of the \( H_2 \), \( HD \), and \( D_2 \) molecules. The corrections were derived through canonical transformation applied to crude adiabatic molecular Hamiltonian. These transformations mix together electrons and phonons (normal coordinate canonical transformation) leading to adiabatic molecular Hamiltonian. Using second quantization formalism and many–body
diagramatic perturbation theory and splitting the adiabatic Hamiltonian into unperturbed part and perturbation we derived the formulae for adiabatic corrections. The results were compared with the obtained by different approaches by Wolniewicz [24] and recently by Kutzelnigg [27]. The quasiparticle canonical transformations were then generalized in a way that electrons and phonons are mixed not only through the normal coordinate but also through the momenta. This canonical transformation leads to non–adiabatic molecular Hamiltonian (motion of electrons does not follow the motion of nuclei, the electrons are phase shifted with respect to nuclei). One can clearly see that the electronic and vibrational motion cannot be separated. The mixed system behaves as one whole quasiparticle (mixed electrons and phonons through the last (momentum) transformation behaves as a renormalized fermions and a different mixture of electrons and phonons leads to renormalized bosons). This in some extent analogous to the introduction of quasiparticles in the solid state theory, where the ”bare” electron interacting with quantized lattice vibrations is renormalized to ”absorb” some part of this interaction, and this quasiparticle is known as a polaron. We were able to derive equations for non–adiabatic \( \tilde{C} \) coefficients, which permits us to calculate the so called mass polarization terms and thus non–adiabatic phonons. It is interesting that the quasiparticles preserves some interesting features known from pure electronic molecular Hamiltonian calculations e.g. we can speak about orbital energies of a new quasiparticles, correlation energies of of a new quasiparticles, Hartree–Fock energy (holes and particles), etc. Further very important property which follow from the last canonical (momentum) transformation is that we clearly see that in the case of electronic quasidegeneracy when \( \tilde{C} \) coefficients are non-negligible (non–adiabaticity is not a small correction) we should work with a full non–adiabatic Hamiltonian. In the case when non–adiabaticity is a small correction and \( \tilde{C} \) coefficients are negligible, we can work with adiabatic Hamiltonian (we have only \( C \) coefficients through CPHF equations) and only if system is perfectly separable that even \( C \) coefficients are negligible we can work with purely electronic Hamiltonian.
ACKNOWLEDGMENTS

This work was supported by the grants 1/4197/97 of the Slovak Grant Agency for Science and 202/98/1028 of the Grant Agency of the Czech Republic.
REFERENCES

[1] M. Born and K. Huang, *Dynamical Theory of Crystal Lattices*, London, Oxford University Press (1956).

[2] H.C. Longuet–Higgins, *Adv. Spectrosc.* **2**, 429 (1961).

[3] H. Köppel, W. Domcke and L. S. Cederbaum, *Adv. Chem. Phys.* **57**, 59 (1984).

[4] S. Wilson, *Electron Correlation in Molecules*, Clarendon Press, Oxford (1984).

[5] B.T. Sutcliffe, *Methods in Computational Chemistry* 4 (S. Wilson, Ed.), p. 33, Plenum Press, New York (1992).

[6] D. Yarkony, *Rev. Mod. Phys.* **68**, 985 (1996).

[7] M. Born and R. Oppenheimer, *Ann. Physik (Leipzig)* **84**, 4357 (1927).

[8] W. Kutzelnigg, *Mol. Phys.* **90**, 909 (1997).

[9] A.S. Davidov, *Quantum Mechanics*, Addison Wesley, New York (1965).

[10] N.C. Handy and A.M. Lee, *Chem. Phys. Lett.* **252**, 425 (1996).

[11] H. Sellers and P. Pulay, *Chem. Phys. Lett.* **103 103**, 463 (1984).

[12] I. Hubač and M. Svrcék *Int. J. Quant. Chem.* **23**, 403 (1988).

[13] I. Hubač, P. Čársky, unpublished results.

[14] M. Wagner, *Phys. Stat. Sol. (b)* **107**, 617 (1981).

[15] M. Wagner, *J. Chem. Phys.* **82**, 3207 (1985).

[16] J.A. Pople, K. Raghavachari, H.B. Schlegel, J.S. Binkley *Int. J. Quant. Chem. Symp* **13**, 225 (1979).

[17] J. Gerratt and J. M. Mills, *J. Chem. Phys.* **49**, 1719 (1968).

[18] J. Gerratt and J. M. Mills, *J. Chem. Phys.* **49**, 1730 (1968).
[19] M. Svrček, *PhD. Thesis*, Faculty of Mathematics and Physics, Bratislava (1986).

[20] I. Hubač and M. Svrček, *Methods in Computational Chemistry* 4 (S. Wilson, Ed.), p.145, Plenum Press, New York (1992).

[21] J. P. Blaizot and G. Ripka, *Quantum Theory of Finite Systems*, The MIT Press Cambridge, Massachusetts, London, England (1986).

[22] I. Hubač, P. Babinec, J. Urban, P. Mach, J. Mášik, M. Polášek, J. Leszczynski, *Asian J. Spectroscopy*, 1 181 (1997).

[23] I. Hubač, M. Svrček, E. A. Salter, C. Sosa and R. J. Bartlett, *Lecture Notes in Chemistry*. Vol. 52, p. 95, Springer, Berlin (1988).

[24] L. Wolniewicz, *J. Chem. Phys.* 99, 1851 (1993).

[25] P.O. Widmark, P.A. Malmqvist, B. Roos, *Theor. Chim. Acta.* 77, 291 (1990).

[26] L.I. Kleinman and M. Wolfsberg, *J. Chem. Phys.* 60, 4740 (1974).

[27] W. Cencek, W. Kutzelnigg, *Chem. Phys. Lett.* 266, 383 (1997).
|       | Wolfsberg [26] | Wolniewicz [24] | Kutzelnigg [27] | Handy [10] | Present method, eq.(87) |
|-------|----------------|-----------------|-----------------|------------|-------------------------|
| $H_2$ | 101.3          | 114.591         | 114.591         | 101        | 136.89                  |
| $D_2$ | 50.7           | 57.296*         | 57.296*         | 50.5*      | 68.62                   |
| $HD$  | 76.0           | 85.943*         | 85.943*         | 75.8*      | 102.67*                 |

*These adiabatic corrections were obtained by reduced mass rescaling from $H_2$ corrections [26].