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Complete error potential*

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The complete error potential is a function of electronic and nuclear coordinates which has to be added to the physical potential in order to obtain the eigenfunctions of the molecular Hamiltonian in an *a priori* specified approximation. This potential is essential for the error theory, in particular it furnishes a simple justification of the Born-Oppenheimer approximation. It is given as a sum of the electronic error potential and that of the intramolecular forces, whose importance is discussed.

Key words: Error potential — Intramolecular forces — Born-Oppenheimer

1. Error theory in quantum chemistry

The error theory for Schrödinger quantum mechanics has been developed since 1953 [1]. Relying on Weinstein's perturbation theory [2], one calculates the error bound step, which leads to the concept of the error potential [3, 4], a trivial and well known concept [5]. The origin of this idea, as well as related methods, are reviewed in [6].

1.1. Electronic error potential

The electronic error potential is defined as

$$V = \psi_{el}^{-1}[E(y) - \hat{H}(x; y)]\psi_{el},$$

where ψ_{el} represents an approximation to the eigenstate of the Hamiltonian $\hat{H}(x; y)$ and $E(y)$ is the mean value of $\hat{H}$ on ψ_{el}. From its form, it is apparent that it establishes a connection between several problems, namely:

1. It provides a physical meaning of the approximation made for ψ_{el}. It is the

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

potential which must be added to the potential appearing in $\hat{H}(x; y)$ in order that ψ_{el} becomes an exact eigenstate.

2. It enables us to calculate the upper bounds for the errors of observables, taking into account the "molecular diagram" [6-9] (which denotes or generalises a first order density matrix).

3. It provides a local test of ψ_{el} in the configuration space as well as in the physical space.

4. It allows for the correction of errors in the structure or in the energy. One can associate an improved solution with each proposed solution [4, 6, 8, 10] leading to an iterative procedure whose convergence is controllable.

5. It establishes the relationship between the correlation error of the wavefunction and the quantum potential of L. de Broglie [11, 12].

[6] gives a brief overview of the developments in the error theory since 1960 [13], including the special forms of the error potential which have been found, and related concepts [14] in particular the pseudo-potentials. "The local error" [15], published in 1985, contains an identical expression to that of the error potential even though derived from another series of concepts [16]. Until now, the theory of the error potential was not formulated for the molecular system consisting of electrons and nuclei; this will be done in this paper.

1.2. The complete error potential

Consider a complete Hamiltonian

$$\hat{H}(x; y) = \hat{T}_y + \hat{H}_e(x; y) = \hat{T}_y + \hat{T}_x + W(x; y) \tag{2}$$

where x represents the electronic configuration, y the nuclear configuration, $\hat{T}$ the operators of kinetic energy, and W the electrostatic potential of the system. Let $\phi(x; y)$ be an approximate eigenfunction of $\hat{H}(x; y)$ considered as a molecular wavefunction. In order that ϕ becomes an eigenfunction of the perturbed Hamiltonian $\hat{H}(x; y) + P(x; y)$, we must take as a perturbation the following expression.

$$P(x; y) = \phi^{-1}(x; y)[H - \hat{H}(x; y)]\phi \tag{3}$$

(H denotes the mean value of $\hat{H}$ on $\phi(x; y)$). $P(x; y)$ will be called the complete error potential. It can be written as a sum of two terms:

$$P^{(no)}(x; y) = \phi^{-1}(x; y)(T_y - \hat{T}_y)\phi \tag{4}$$

and

$$P^{(el)}(x; y) = \phi^{-1}(x; y)[H_e - \hat{H}_e(x; y)]\phi \tag{5}$$

(the quantum mean values on ϕ are designated by suppressing the caret).

2. Calculation of the error resulting from the Born–Oppenheimer separation

According to the Born-Oppenheimer theorem (in the following abbreviated as BO) an approximation of the molecular wavefunction is given by

$$\phi_{n,\nu}(x; y) = \psi_n(x; y)\Theta_{n,\nu}(y) \tag{6}$$

where n designates the set of quantum numbers associated with the state of the system of electrons, ν the set of quantum numbers associated with the state of the nuclear framework; $\psi_n(x; y)$ and $\Theta_{n,\nu}(y)$ as well as the corresponding eigenvalues $E_n(y)$ and $\omega_{n,\nu}$ are defined by Eqs. (7) and (8), respectively, using $\hat{H}_e(x; y)$ defined in Eq. (2).

$$\hat{H}_e(x; y)\psi_n(x; y) = E_n(y)\psi_n(x; y) \tag{7}$$

$$[\hat{T}_y + E_n(y)]\Theta_{n,\nu}(y) = \omega_{n,\nu}\Theta_{n,\nu}(y). \tag{8}$$

Let us calculate, for the function ψ given by Eq. (6), the second term $P_n^{(el)}$ (Eq. 5), of the complete error potential, taking into consideration Eq. (7).

$$H_e = \langle \psi_n(x; y)\Theta_{n,\nu}(y) | \hat{H}_e(x; y) | \psi_n\Theta_{n,\nu} \rangle = \langle \psi_n\Theta_{n,\nu} | E_n(y) | \psi_n\Theta_{n,\nu} \rangle = \langle E_n(y) \rangle$$

$$\phi_{n,\nu}^{-1}(x; y)\hat{H}_e(x; y)\phi_{n,\nu}(x; y) = \psi_n^{-1}(x; y)\Theta_{n,\nu}^{-1}(y)\hat{H}_e(x; y)\psi_n\Theta_{n,\nu}$$

$$= \psi_n^{-1}\Theta_{n,\nu}^{-1}E_n(y)\psi_n\Theta_{n,\nu} = E_n(y) \tag{9}$$

$$P_n^{(el)}(y) = \langle E_n(y) \rangle - E_n(y). \tag{10}$$

This term depends only on the nuclear configuration y. In particular for the equilibrium configuration y_{eq}, the energy reaches its minimum $E_n^{(min)}$ and thus

$$P_n^{(el)}(y_{eq}) = \langle E_n(y_{eq}) \rangle - E_n^{(min)}. \tag{11}$$

To evaluate the term $P_n^{(no)}$ in Eq. (4), we observe: if $y = (y^{(i)})$, then

$$\psi_n(x; y) - \psi_n(x; y_{eq}) = \sum_i [y^{(i)} - y_{eq}^{(i)}]\frac{\partial}{\partial y^{(i)}}\psi_n(x; y_q)$$

where $y_q^{(i)} \in [y_{eq}^{(i)}, y^{(i)}]$. The expression in [ ] is small in the vicinity of the equilibrium; the other factors, proportional to the momenta, decreases with increasing nuclear mass. Therefore

$$\psi_n(x; y) \approx \psi_n(x; y_{eq}). \tag{12}$$

Following Eqs. (12) and (8), we have

$$T_y \approx \langle \psi_n(x; y)\Theta_{n,\nu}(y) | \hat{T}_y + E_n(y) | \psi_n(x; y_{eq})\Theta_{n,\nu}(y) \rangle$$

$$- \langle \phi_n(x; y) | E_n(y) | \phi_n \rangle = \omega_{n,\nu} - \langle E_n(y) \rangle,$$

$$\phi^{-1}\hat{T}_y\phi_n(x; y) \approx \omega_{n,\nu} - E_n(y),$$

$$P_n^{(no)} \approx E_n(y) - \langle E_n(y) \rangle. \tag{13}$$

Considering approximation (12), the expression for $P_n^{(no)}$, Eq. (13), is the negative of the expression for $P_n^{(el)}$, Eq. (10), for arbitrary n, thus

$$P_n = P^{(el)} + P_n^{(no)} \approx 0. \tag{14}$$

The use of the complete error potential made this calculation very simple. At the same time, it showed that there is a compensation between the errors coming from the kinetic energy of nuclei on the one hand, and from the electronic Hamiltonian on the other. Finally, it indicated that the residual error is due to the modification of the electronic wavefunction as either we move away from the equilibrium, or the nuclei are made lighter.

3. Complete error potential due to the approximation of the electronic wavefunction

The methods for finding the electronic wavefunction $\Gamma_n(x; y)$ usually generate an error, as indicated by the following eigenvalue equation

$$[\hat{H}_e(x; y) + V_n(x; y)]\Gamma_n(x; y) = [E_n(y) + \Delta E_n(y)]\Gamma_n(x; y). \tag{15}$$

Expression (16) for the complete wavefunction will replace expression (6) thus enabling the calculation of the complete error potential.

$$\phi_{n,\nu}^{(app)}(x; y) = \Gamma_n(x; y)\Theta_{n,\nu}^{(app)}(y). \tag{16}$$

Equation (7) is replaced by Eq. (17) defining ΔE_n, as an increase in the electronic energy due to the error

$$[\hat{H}_e(x; y) + V_n(x; y)]\phi_{n,\nu}^{(app)}(x; y) = [E_n(y) + \Delta E_n(y)]\phi_{n,\nu}^{(app)}(x; y) \tag{17}$$

The calculation of the expression (7) for $P_n^{(el)}$ is modified as follows

$$\begin{aligned}
H_e^{(app)} &= \langle \Gamma_n(x; y)\Theta_{n,\nu}^{(app)}(y)|H_e(x; y)|\Gamma_n\Theta_{n,\nu}^{(app)}\rangle \\
&= \langle \Gamma_n(x; y)\Theta_{n,\nu}^{(app)}(y)|E_n(y) + \Delta E_n(y) - V_n(x; y)|\Gamma_n\Theta_{n,\nu}^{(app)}\rangle \\
&= \langle E_n(y)\rangle + \langle \Delta E_n(y)\rangle - \langle V_n(x; y)\rangle. \tag{18}
\end{aligned}$$

We therefore obtain (the last Dirac bracket, which is zero, being written as a reminder).

$$P_n^{(el)}(y) = \langle E_n(y)\rangle - E_n(y) + \langle \Delta E_n(y)\rangle - \Delta E_n(y) + V_n(x; y) - \langle V_n(x; y)\rangle. \tag{19}$$

On the other hand, the expression for $P_n^{(no)}$, Eq. (13), remains unchanged in view of the approximation (12). Hence, we finally have

$$P_n \approx I_n(y) + V_n(x; y) \tag{20}$$

where

$$I_n(y) = \langle \Delta E_n(y)\rangle - \Delta E_n(y). \tag{21}$$

3.1. Potential of intramolecular forces

The term $I_n(y)$ may be considered as a potential in the nuclear configuration space. It implies intramolecular forces

$$F_J^{(n)} = -\frac{\partial I_n(y)}{\partial R_J}, \tag{22}$$

(the intramolecular forces were independently defined [23-28] on the basis of a partition of the total electronic energy). We can draw equipoential lines of $I_n(y)$. We shall let the molecular approach its equilibrium configuration (nonrelativistic) by applying the perturbation $-I_n(y)$.

The terms I_n and F_J have physical meanings provided $\Delta E_n(y)$ is given one. If we neglect the ionic energy, then ionic forces appear, if we neglect the correlation energy, correlation forces appear; if we neglect the formation energy of a super-molecule, intermolecular forces appear (we could also say "intrasupermolecular forces").

Intramolecular forces are often considered [17-19]. One of us has contributed to the following approaches: intra-atomic forces [20], intramolecular electrostatic forces [20-22], and since 1983 correlation forces [23-28]. The definition of the potentials $I_n(y)$ generalizes these later developments. The molecular model of forces is consistent with the representation of the molecular environmental effects by external forces.

3.2. Correlation as an example [23-28]

For a theoretical discussion, it is necessary to consider a starting configuration which contains the entire correlation error, i.e. the wavefunction with doubly occupied orbitals having minimal energy. This configuration must be perturbed in the opposite sense from the complete error potential $P_n(x; y)$. The term $-I_n(y)$ moves the nuclei in the direction of the intramolecular correlation forces. The term $-V_n(x; y)$ modifies the electronic configuration, which can only be realized by the creation of partial holes in the occupied orbitals and by the partial occupation of unoccupied orbitals [29]. This can be compared with a statistical redistribution of the populations in the energy levels [25-27]: The levels which are almost completely occupied simulate a condensed phase while the levels which are almost empty simulate a gas phase, which is in equilibrium with the condensed phase. The excitation from bonding orbitals to antibonding orbitals simulates a pressure. This simplified picture of intramolecular vaporization permits the prediction of a preference for dilation and symmetrisation, which becomes exact if we analyse $I_n(y)$. The electronic error potential $V_n(x, y)$ and the potential of the correlation forces describe the same global phenomenon. Nevertheless, the situation varies for different molecules and the correlation may be analyzed in various ways [27, 28].

4. Conclusion

We have defined the complete error potential for a molecule. We limited ourselves to the nonrelativistic case. This complete error potential is expressed as a sum of the electronic error potential and the potential of the intramolecular forces. This complete error potential generalizes the properties of the electronic error potential and explains the molecular model of forces.

With the use of this potential it is finally possible to evaluate and to discuss the Born-Oppenheimer approximation and in particular the specific behaviour of hydrogen nuclei.

References

1. Laforgue A (1953) CR Acad Sci 236:202
2. Weinstein DH (1934) Proc Nat Acad Sci 20:529
3. Laforgue A (1954) CR Acad Sci 238:1033
4. Laforgue A (1954) Thèse Paris; (1954) Cah Phys 57-58:25; (1954) ibid 59:16; (1954) ibid 63:18; (1955) ibid 64:41

5. Laforgue A (1956) L'analyse de l'erreur liée à la construction des fonctions d'onde approchées en théorie de la matière, Cours libre à la Faculté des Sciences, Paris; (1960 et sq.) Mécanique Ondulatoire et Chimie Quantique, Cours de 3ème cycle, Faculté des Sciences, Lyon; (1969) Calcul d'erreur en Mécanique quantique, Cours de 3ème cycle, Faculté des Sciences, Lyon; (1980) Mécanique quantique Cours de 1er cycle, Faculté des Sciences, Reims
6. Laforgue A (1985) Can J Chem 63:1788
7. Daudel R, Laforgue A (1951) CR Acad Sci 233:623; (1951) 233:1608
8. Laforgue A (1957) J Chim Phys 54:413
9. Koutecky J, Laforgue A (1977) Int J Quantum Chem 11:505
10. Laforgue A (1959) Cah Phys 112:495
11. Laforgue A (1957) Ann Fac Sci Saïgon 7
12. Laforgue A (1958) Colloque sur le calcul des fonctions d'onde moléculaires, p 157, CNRS, Paris
13. Alexander MN (1969) J Chem Phys 51:5660
14. Preuss H (1969) Acta Phys Acad Sci Hung 27:191
15. Casida M (1985) Int J Quantum Chem 27:451 and references therein
16. King FW, Le Gore MA and Kelly MK (1981) J Chem Phys 75:809 and references therein
17. Sinanoglu C (1983) Adv Chem Phys 6:315 (see, for instance, pp 399–400)
18. Burkert U, Allinger NL (1982) Molecular mechanics. Am Chem Soc monograph no 177, Washington DC
19. Gresh N, Claverie P, Pullman A (1983) Theor Chim Acta 66:1; Gresh N, Pullman A, Claverie P, (1985) Theor Chim Acta 67:11
20. Laforgue A, Vroelant C, Masse JL (1955) CR Acad Sci 24:1265
21. Laforgue A, Theophanides T (1974) J Mol Struc 22:125
22. Laforgue A, Bruceña-Grimbert C, Laforgue-Kantzer D, Del Re G, Barone V (1982) J Phys Chem 86:4436
23. Laforgue A (1985) J Mol Struct Theochem 120:241
24. Laforgue A, Roszak S (1983) CR Acad Sci Ser II 297:459
25. Laforgue A, Jbara O (1985) Ve Congrès int de Chimie quantique, Montréal, Résumés, p 60
26. Laforgue A, Jbara O (1985) CR Acad Sci Sér II 301:1179
27. Laforgue A, Varandas AJC (1986) CR Acad Sci Sér II 302:395
28. Laforgue A, Guérin P (1987) WATOC Congress, Budapest. Intramolecular correlation forces (Poster communication)
29. Laforgue A, Paldus J, Cizek J (1973) J Chem Phys 59:2560
30. Laforgue A, Roland S, Ammar M (1974) Ann Université et ARERS Reims 12:1