

Simulation Techniques in Parametric Hamiltonians

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Using simulation techniques, a general definition of parametric Hamiltonians (H_{pa}), is presented. The minimal distance between a parametric and the exact Hamiltonian (H_{exa}) is defined in terms of the sum of the least distance between the corresponding energy functional components. A reference electronic energy functional for simulation of H_{exa} is proposed based on a CI energy functional. General properties of parametric Hamiltonians are analyzed considering reduction of the number of particles, integrals, and basis set, elimination of orthogonal transformations, and correlation and total energy functionals. Parametric Hamiltonians based on simulation of binding energy functionals and a simple parametrization scheme are proposed. Some preliminary tests have been performed with the parametrization of a characterized H_{pa} and calculations of organic (CH_4 , C_2H_2 , C_2H_4 , and C_2H_6) and transition metal (Ni_2 and Ni_5) systems.

1. INTRODUCTION

Due to many technological problems involved in the study materials properties, the development of theoretical methods that are able to evaluate the physical and chemical characteristics of these materials is of paramount importance.^{1–6} Therefore, the understanding, optimization, and elaboration of well-defined approximate Hamiltonians are of interest.⁷

Highly accurate methods normally reach impractical limits even for small molecules of very heavy atoms. The inclusion of correlated wave functions in the calculation of physical observables is fundamental in the description of electronic properties of systems with transition metal atoms. In addition, most of the complex systems require the modeling of a variety of complicated processes, each of them involving a huge amount of calculations. For example, in catalytic processes, surface reactions occur through several steps that involve active sites (some times associated to excited states), reaction barriers (transition states for diffusion, segregation, chemical reaction, etc.), surface relaxation, cooperative effects, weak interactions, etc. Each of them demands an enormous computational effort even for single point calculations. For this reason, approximate methods that allow modeling of chemical systems close in size to reality are indeed indispensable.

In spite of the large amount of work in the area of approximate Hamiltonians,^{1–10} few methodological approaches aimed at the development of new parametric Hamiltonians have been performed. Approximate quantum mechanical methods are necessary for simulation of amorphous and complex systems that contain transition metals and other heavy atoms. The qualitative and semiquantitative simulation of material properties is central in the experimental research of many technological problems. For this

reason, the development and implementation of general formalisms and strategies to reach systematic improvements of parametric methods in quantum chemistry is relevant.

In this work an examination of parametric Hamiltonians based on simulation techniques is performed in section 2, emphasizing in the strategy of minimizing the distance between Hamiltonian components. A discussion of the energy functional and the reference Hamiltonian is included in section 3, considering the exact energy from configuration interaction approach. A short review of approximations and examples of functionals in parametric Hamiltonians, including electronic correlation, is presented in section 4. In addition, a general viable procedure to define parametric Hamiltonians is proposed in section 5 by considering the simulation of the binding energy functionals from diatomic molecules. Finally, in section 6, simple tests for the parametrization and calculation of small molecules have been carried out to validate some of the discussed strategies.

The main purpose of this work is to establish a criterion to define parametric Hamiltonians in a very simple manner, using simulation techniques¹¹ based on a reference CI Hamiltonian energy functional instead of a more complicated development from perturbation theory.⁴ Quantum parametric methods have been early established as emulation of the HF method in which parameters take care of correlation effects. The key point is that the simulation is not only in the Hamiltonian but also in the basis set, through the representation of the Hamiltonian matrix elements by parametric functionals defined at different internuclear distances. For example, a straightforward description of dynamic correlation energy functional used in standard semiempirical methods is obtained from the simulation of a CI Hamiltonian. Thus, the simulation of energy components, as has been shown elsewhere,¹² can be used as a convenient strategy to select new parametric functionals. Simulation techniques are also used to define a general and simple parametrization procedure based on references that can be dissociation energy,

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excitation energy, and heat of formation. Very simple examples using dissociation energies from diatomic molecules and the calculation of small molecules with light and heavy (transition metal) atoms also was performed to test the proposed parametrization procedure based on simulation techniques.

2. SIMULATION TECHNIQUES

According to Barthelat and Malrieu¹¹ emulation of Hamiltonians can be formally established using properties of the Liouville space. In particular, simulation¹³ and generalized least squares techniques¹⁴ can be used to define parametric Hamiltonians (H_{pa}). These Hamiltonians do not only comprise the semiempirical type but those defined from parameters obtained from accurate theoretical calculations.

Given a trial parametric Hamiltonian family F , the optimal H_{pa} that belongs to that family may be determined by the minimization of the distance between H_{exa} and H_{pa} , that is,

$$\min_{H_{pa} \in F} \|H_{exa} - H_{pa}\| = \min_{H_{pa} \in F} \left(\sum_{I, J \in S} |(\phi_I, H_{exa} \phi_J) - (\phi_I, H_{pa} \phi_J)|^2 \right)^{1/2} \quad (1)$$

where ϕ_I belongs to a complete orthonormal set of eigenfunctions $\{\phi_k\}$ of H_{exa} that expands a S subspace of the Hilbert space. The symbols (\cdot, \cdot) and $\|\cdot\|$ mean inner product and norm function, respectively.

The exact n -particle Schrödinger equation solution can be expanded in terms of a complete orthogonal basis set $\{\phi_\mu\}$,¹⁵ and H_{exa} and H_{pa} operators may be expressed in terms of simpler operators, ($H_\alpha = \sum_n H_{\alpha n}$, $\alpha = exa, pa$), for example, one-particle (kinetic energy and nucleus-electron attraction) or the two-particle (electron-electron repulsion) operators. Therefore, a sufficient and not necessary condition for the minimization of the distance between Hamiltonian operators may also involve minimization of the correspondent components

$$|(\phi_\mu, (H_{exa_n} - H_{pa_n}) \phi_\nu)|_{\min} \quad (2)$$

in which H_{exa_n} are $1/2\Delta_1$, $Z_A/(|x_1 - R_A|)$, and $1/(|x_1 - x_2|)$.

Although the minimal distance obtained from eq 1 is not of the same magnitude as that calculated from the sum of the component minimal distances (triangular inequality for normed linear spaces, $\|x-y\| \leq \|x-z\| + \|z-y\|$), the optimal values from eq 2 will also minimize expression 1 in the sense that if $\|x-z\| \rightarrow 0$ and $\|z-y\| \rightarrow 0$, $\Rightarrow \|x-y\| \rightarrow 0$. The energy components can be grouped, and error cancellations can be exploited as an advantage; nevertheless, the physical meaning of energy terms can be missed and an analysis of energy partition^{16,17} and a study of the behavior of each functional with the internuclear distance cannot be accomplished.¹² Clementi and Corongiu using the HFCC method¹⁶ have successfully explored the strategy of defining convenient parametric functionals by considering the analysis of energy components.

Usually parametric Hamiltonians are unknown; instead, an operator matrix representation is used $(\phi_\mu, H_{pa_n} \phi_\nu)$ expressed in terms of functions and functionals based on parameters. Note that in parametric Hamiltonians the simula-

tion of each energy component involves values of the functionals at different nuclear coordinates $\{C_{XY}\}$ considering the Born–Oppenheimer Hamiltonian. This means that multicenter functionals are functions of $\{C_{XY}\}$ and implicitly include different optimal basis sets at different internuclear distances in the molecular system.

3. ENERGY FUNCTIONAL FOR SIMULATION

It is important beforehand to know in some detail expressions for electronic energy functionals in relation to the simulation of approximate Hamiltonians. The energy expression for H_{exa} can be analyzed considering the non-relativistic case and the nuclear-electron decoupling in the Born–Oppenheimer approach. In this case, the configuration interaction (CI) electronic energy E_e is obtained by employing the intermediate normalization technique.¹⁵

$$E_e = \sum_{\mu, \nu} \left[P_{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\lambda, \sigma} P'_{\mu\nu} P'_{\lambda\sigma} \left((\mu\lambda, \nu\sigma) - \frac{1}{2} (\mu\lambda, \sigma\nu) \right) \right] \quad (3)$$

where

$$P'_{\mu\nu} P'_{\lambda\sigma} = P_{\mu\nu} P_{\lambda\sigma} + 2C_{\mu\nu\lambda\sigma} \quad (4)$$

and

$$C_{\mu\nu\lambda\sigma} = \sum_{b>a, s>r} C_{ab}^{rs} C_{\mu_a}^* C_{\eta_r} C_{\lambda_b}^* C_{\sigma_s} \quad (5)$$

and $P_{\mu\nu} = \sum_i C_{\mu i} C_{\nu i}$ is a density matrix element. The $h_{\mu\nu}$ and $(\mu\lambda, \nu\sigma)$ terms correspond to the core Hamiltonian and two-electron interaction integrals over atomic orbitals, respectively. The C_{ab}^{rs} terms are double-excitation CI coefficients obtained from a full-CI calculation.

The electronic energy functional is, in some sense, structurally similar to the HF one. The difference is essentially in the $P'_{\mu\nu}$ terms that depend on configuration interaction (C_{ab}^{rs}) and occupied ($C_{\mu_a}^*$ and $C_{\lambda_b}^*$) and unoccupied molecular orbitals (C_{ν_r} and C_{σ_s}) coefficients as shown in eq 5. That is, the E_e can be expressed basically as the sum of the core Hamiltonian, Coulomb, and exchange integrals. In the HF case the later integrals are weighted by a product of density matrix elements ($P_{\mu\nu} P_{\lambda\sigma}$) while in the correlated energy functional the weighted factor ($P_{\mu\nu} P_{\lambda\sigma} + 2C_{\mu\nu\lambda\sigma}$) includes a correction to compensate the overestimation of the repulsive interelectronic interaction due to an uncorrelated electronic density.

A more practical way to visualize E_e is by considering a correction in the electron–electron interaction integrals¹⁸ and not in the density terms

$$E_e = \sum_{\mu, \nu} \left[P_{\mu\nu} h_{\mu\nu} + \frac{1}{2} \sum_{\lambda, \sigma} P_{\mu\nu} P_{\lambda\sigma} \left((\mu\lambda, \nu\sigma)' - \frac{1}{2} (\mu\lambda, \sigma\nu)' \right) \right] \quad (6)$$

where

$$(\mu\lambda, \nu\sigma)' = (\mu\lambda, \nu\sigma) + [2C_{\mu\nu\lambda\sigma}/P_{\mu\nu} P_{\lambda\sigma}] (\mu\lambda, \nu\sigma) \quad (7)$$

is named pair-correlation energy.

Thus,

$$E_e = E_{\text{HF}} + \sum_{\mu,\nu} \sum_{\lambda,\sigma} P_{\mu\nu} P_{\lambda\sigma} C'_{\mu\nu\lambda\sigma} \left((\mu\lambda, \nu\sigma) - \frac{1}{2} (\mu\lambda, \sigma\nu) \right) \quad (8)$$

where $C'_{\mu\nu\lambda\sigma} = [2C_{\mu\nu\lambda\sigma}/P_{\mu\nu}P_{\lambda\sigma}]$.

An obvious practical question emerges from the above analysis: Is it viable to simulate an exact Hamiltonian with a parametric one that has a similar energy functional? The answer is yes. The problem is whether the chosen functional is feasible to be managed in a pragmatic way. According with eqs 3 and 8, it is possible to simulate an accurate energy functional using a CI wave function. However, simulation of extended basis in post-HF approaches can be impractical even for small systems. Nevertheless, in principle, a base transformation exists whereby the exact solution can be expressed in terms of a small basis set. This basis (optimal transformed minimum basis set OTMBS) is unknown and is implicitly included in the energy component functionals. The optimal energy functional for a very small basis set would be that of eq 8 but with a finite basis. Note that in a simulated HF approach, used as reference for a CI, the Coulomb and exchange integrals $(\mu\lambda, \sigma\nu)$ are assumed to be calculated in the OTMBSs. The correlation energy (dynamic) is normally added as an average through functionals that simulate the second term in expression 8, as shown in previous work.¹² In addition, functionals for the two-center Coulomb integrals using, for example, the Ohno-Klopman approximation¹⁹ and the adjustment procedure of Dewar-Sabelli²⁰ in MINDO/3²¹ also include part of the electronic correlation (interatomic correlation²²). On the other hand, due to limitations of the single-determinantal wave function (for example, symmetry breaking) nondynamic correlation may be included by considering a small active space using multireferences or by fractional occupation numbers.

Several points must be kept in mind before continuing the discussion of parametric functionals. Orbital coefficients obtained in the diagonalization of the Fock matrix equation do not correspond to the used basis set. As pointed out above, the components of the matrix elements of the transformed Hamiltonian are represented in terms of functionals that depend on parameters and correspond to an unknown basis set. Instead the basis set employed is used to give a qualitative information through orbital representation and in some cases to built up functionals such as those that appear in the Mulliken approximation for the resonance integral.²³

As it is well known, one of the weaknesses of the earlier semiempirical methods is that the parametrization was carried out with respect to the HF approach which does not include the correlation between electrons of different spin. The inclusion of this correction is indispensable to evaluate chemical processes that lead to dissociation, bond formations, and excitations, even more for molecular systems that contain transition metals. Thiel has early established this assertion in the application of parametrical methods (MNDO and MNDOC²⁴) to molecular systems with specific correlation effects, such as transition and excited states of organic molecules. One of the advantages of parametrizing functionals with respect to accurate experimental data is the inclusion, in some respect, not only of the electronic correlation but also relativistic effects and electron-nucleus coupling movement, which are difficult to evaluate in

theoretical calculations. The main problem is that, in many cases, experimental data is not available; therefore, parametrization has to be performed with respect to the most accurate theoretical calculations.

4. FUNCTIONALS IN PARAMETRIC HAMILTONIANS

The total energy functional ($E_t = E_e + E_n$) of H_p is represented as parametric functionals in both the electronic (E_e) and the nuclear (E_n) terms. This requirement is of great practical computational importance, particularly on complex systems that contain transition metals, in which effective core potential and electronic correlation are included in an implicit way. In order to reach efficient, operative, and judicious parametric methods, several involved approaches are demanded: reduction of the number of particles, integrals, and basis set and elimination of matrix transformations.

In the first case, the simplification is carried out by freezing the core electrons or using model potentials introduced through energy component functionals that also simulate the less active electrons (core electrons). In this way, the number of equations to be solved is reduced in a considerable way particularly for transition metal systems. A fundamental justification of this approach is given by Huzinaga.²⁵ The second approach reduces the number of calculated integrals based on the application of the well known zero differential overlap approximation (ZDO).²⁶ The conceptual considerations of this approximation has been recently revised and explained by Neymeyr and Seelig.²⁷ The third simplification related with the basis-set size is achieved not only by the two previous approaches but also by the use of a minimal basis set. In the fourth approach, the evaluation of the transformed F matrix back and forth through the SCF process is avoided, because the basis set is assumed orthogonal and therefore the overlap matrix is postulated to be diagonal, leading to a matrix equation $F'C' = C'\epsilon$. Note that in this case the Fock matrix elements are evaluated with parametric functionals in an unrecognizable basis set and with an unknown orthogonalization procedure. The type of orthogonalization used may be relevant, because it must obey symmetry restrictions for each functional.

In parametric methods, the electronic Hamiltonian operator is represented in a matrix form in terms of a minimum basis set; for example, the Hartree-Fock operator ($H_{\text{HF}} = \sum_i f_i$, where f_i is the one-particle HF operator) can be written as

$$H_{\text{HF}} = \begin{pmatrix} F_{11} & F_{12} & \dots F_{1k} & \dots & F_{1n} \\ F_{21} & F_{22} & \dots F_{2k} & \dots & F_{2n} \\ \cdot & \cdot & \dots & \dots & \cdot \\ \cdot & \cdot & \dots & \dots & \cdot \\ F_{n1} & F_{n2} & \dots F_{nk} & \dots & F_{nn} \end{pmatrix} \quad (9)$$

where

$$F_{\mu\nu} = (\phi_\mu, H_{\text{HF}} \phi_\nu); \quad \mu, \nu = 1, 2, \dots, n \quad (10)$$

The number of terms to handle in these expressions is too large for systems of chemical interest. For example, the number of integrals $(\mu\lambda, \nu\sigma)$ to be calculated in the HF approach is of the order of n^4 , where n is the number of basis. Therefore, for an all-electron calculation of a transition metal diatomic molecule with a reasonable basis set (100 functions), it is necessary to evaluate about 10^8 integrals. In the case of semiempirical methods, the number of terms in

(9) is reduced to $(n - n_c)^2$ integrals (n_c = number of basis for core electrons) when the ZDO and frozen core approximations are applied. The efficiency of a SCF parametric Hamiltonian with respect to several methods has been well established in Table 1 of ref 1d.

The two-center correlation energy in expression 8 is simulated in some semiempirical methods (for example MINDO/3²¹) by functionals, such as¹²

$$\sum_{X>Y} -Z_X Z_Y f(R_{XY}, \alpha_{XY}) \gamma_{XY} \quad (11)$$

This expression can be deduced after applying the ZDO approximation²⁶ to the last term in expression 8; this is transformed in

$$\sum_{X>Y} \sum_{\mu}^X \sum_{\lambda}^Y P_{\mu\mu} P_{\lambda\lambda} C'_{\mu\lambda}(\mu\lambda, \mu\lambda) \quad (12)$$

If $(\mu\lambda, \mu\lambda)$ integrals and $C'_{\mu\lambda}$ are assumed to be the same for μ and λ belonging to the same pair of atoms (i.e., $\mu \in X$ and $\lambda \in Y$, $X \neq Y$), they can be approximated by γ_{XY} and $f(R_{XY}, \alpha_{XY})$, respectively. Here, γ_{XY} corresponds to a function of R_{XY} that represents an average value of $(\mu\lambda, \mu\lambda)$ integrals. The $-f(R_{XY}, \alpha_{XY})$ term is an exponential or Gaussian function that depends on the adjusted parameter α_{XY} and decreases in absolute value with the increase of the internuclear distance R_{XY} . Note that the negative value of this term accounts for the correction of the electronic energy in expression 8; i.e., the CI electronic energy must be more negative than the HF one. Finally, the $\sum_{\mu}^X P_{\mu\mu}$ terms are approximated as the corresponding nucleus core charge (Z_X).

The nature of parametric functionals can be easily visualized by the matrix elements of a H_{pa} Hamiltonian such as PM3²⁸

$$F_{\mu\mu}^{(PM3)} = U_{\mu\mu} + \sum_{X(\neq Y)} V_{\mu\mu}^X - \sum_{\nu} P_{\nu\nu}((\mu\nu, \mu\nu) - 1/2(\mu\mu, \nu\nu)) + \sum_{X} \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma}(\mu\lambda, \mu\sigma) \quad (13)$$

$$F_{\mu\nu}^{(PM3)} = H_{\mu\nu} + 1/2 P_{\mu\nu}(3(\mu\mu, \nu\nu) - (\mu\nu, \mu\nu)) + \sum_{X} \sum_{\lambda} \sum_{\sigma} P_{\lambda\sigma}(\mu\lambda, \mu\sigma) \quad (\mu, \nu \in X) \quad (14)$$

$$F_{\mu\nu}^{(PM3)} = 1/2(\beta_{\mu} + \beta_{\nu})S_{\mu\nu} - 1/2 \sum_{\lambda\sigma} P_{\lambda\sigma}(\mu\lambda, \nu\sigma) \quad (\mu \in X \text{ and } \nu \in Y, X \neq Y) \quad (15)$$

where

$$U_{\mu\mu} = \left(\mu, \left(-\frac{1}{2}\Delta - Z_X/r_{X1} \right) \mu \right) = -\frac{1}{2}(I_{\mu} + A_{\mu}) + \left(\frac{1}{2} - Z_X \right) G_{\mu\mu} \quad (16)$$

and $S_{\mu\nu} = (\mu, \nu)$ is the overlap integral.

Table 1. Parameters α_{XY} and β_{XY} from Diatomic Molecules (H_2 , CH, C_2 , and Ni_2) Using Different Core–Core Functionals

diatomic molecule	binding energy (kcal/mol)	bond distance (Å)	α parameter (au)	β parameter (au)	energy gradient (au)
H–H	−104.208 −104.207 ^c	0.74116	(1.621037) [1.512641] {0.006836}	(0.288424) [0.262469] {0.312307}	(3×10^{-18}) $[3 \times 10^{-17}]$ $\{3 \times 10^{-18}\}$
C–H	−79.987 −80.0 ^c	1.1202	(1.393662) [2.524437] {0.345703}	(0.304584) [0.272909] {0.325558}	(3×10^{-4}) $[3 \times 10^{-4}]$ $\{2 \times 10^{-4}\}$
C–C	−144.049 −144.0 ^c	1.2425	(1.260703) [3.105184] {0.437927}	(0.307893) [0.279916] {0.355609}	(3×10^{-5}) $[3 \times 10^{-5}]$ $\{3 \times 10^{-5}\}$
Ni–Ni ^b	−54.43 −55.5 ^c	2.477	1.0688199	0.282541	(8×10^{-4})

^a Values in (), [], and { } correspond to the nuclear repulsion energy functionals: (A) $E_n = Z_X Z_Y ((ss', ss') + (1/R_{XY} - (ss', ss'))\alpha_{XY} e^{-R_{XY}})$; (B) $E_n = Z_A Z_B ((ss', ss') + (1/R_{XY} - (ss', ss'))\alpha_{XY} e^{-R_{XY}})$; and (C) $E_n = Z_X Z_Y ((ss', ss') + (1/R_{XY} - (ss', ss'))\alpha_{XY} e^{-R_{XY}})$, respectively. ^b (D) $E_n = Z_X Z_Y (C_d(ss', ss') + (1/R_{XY} - C_d(ss', ss'))\alpha_{XY} e^{-R_{XY}})$ ($C_d = 1.03$). ^c Experimental values obtained from ref 32.

$$E_n(X-Y) = Z_X Z_Y (ss', ss') (1 + e^{-\alpha_X R_{XY}} + e^{-\alpha_Y R_{XY}}) + Z_X Z_Y / R_{XY} \sum_i^2 (a_{iX} e^{-b_{iX}(R_{XY}-c_{iX})^2} + a_{iY} e^{-b_{iY}(R_{XY}-c_{iY})^2}) \quad (17)$$

Considering the E_n and E_e PM3 components of the total energy, a system of m different type of atoms depends on several parameters as follows

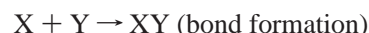
$$E_t = f(\varpi_1, \dots, \varpi) \quad (18)$$

where $\varpi_i = \{U_{ss}, U_{pp}, \beta_s, \beta_p, \xi_s, \xi_p, \alpha_i, G_{ss}, G_{sp}, G_{pp}, G_{p2}, H_{sp}, a_1, b_1, c_1, a_2, b_2, c_2\}_i$ ($i = 1, \dots, m$) is a set of parameters for each element in which ξ_{μ} is the exponent of the orbital μ , $G_{\mu\mu} = (\mu\mu, \mu\mu)$ ($\mu = s, p$), $H_{sp} = (sp, sp)$, and $G_{p2} = (pp, p'p')$.

5. SIMULATION TECHNIQUES AND BINDING ENERGY FUNCTIONALS

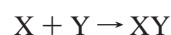
As mentioned in section 2, H_{pa} Hamiltonians are based on functionals that depend on parameters. The value of parameters and the type of functionals may be obtained by simulation techniques with respect to highly accurate calculations or experimental data from molecular and atomic systems.

A straightforward strategy could be to parametrize with respect to energies involved in excitations and bond formations in an atom and a molecule or in a series of molecules



where X and Y may be atoms or molecular fragments.

If the main interest is on parametric Hamiltonians that simulate the energetics of chemical reactions, the most simple example corresponds to a diatomic molecule XY, for which the binding energy (BE^{XY}) has been calculated in a precise way or obtained from experiments. That is, the energy involved in the process



is well-known and is defined as

$$BE^{XY} = E^{XY} - (E^X + E^Y) \quad (19)$$

Each component of this reaction has associated a corresponding wave function and a Hamiltonian:

$$H^{XY}\phi^{XY} = E^{XY}\phi^{XY}; \quad H^X\phi^X = E^X\phi^X; \quad H^Y\phi^Y = E^Y\phi^Y \quad (20)$$

If Hamiltonians and energies of XY molecule are substituted in eq 1, the following expression is obtained:

$$\min||H_{\text{exa}}^{XY} - H_{\text{pa}}^{XY}|| = \min(\sum_{\text{IES}} |E_I^{XY} - E_{\text{pa}_i}^{XY}|^2)^{1/2} \quad (21)$$

Adding and subtracting the $(E^X + E^Y)$ term in the right side of eq 21 results in the following expression

$$\min||H_{\text{exa}}^{XY} - H_{\text{pa}}^{XY}|| = \min(\sum_{\text{IES}} |BE_I^{XY} - BE_{\text{pa}_i}^{XY}|^2)^{1/2} \quad (22)$$

$$BE_{\text{pa}_i}^{XY} = E_{\text{pa}_i}^{XY} - (E^X + E^Y) = (\phi^{XY}, H_{\text{pa}_i}^{XY} \phi^{XY}) - ((\phi^X, H^X \phi^X) + (\phi^Y, H^Y \phi^Y))$$

where BE_I^{XY} and $BE_{\text{pa}_i}^{XY}$ are respectively the binding energies of the XY molecule in I state from experimental data and calculated by the parametric Hamiltonian. Note that the simulation of the energy functional has been transformed to a simulation of a binding energy functional, and it is assumed that the atomic Hamiltonians H^X and H^Y have been correctly simulated.

In practice only a few binding energies (BE_I^{XY}) are well known. In most of the cases, solely the ground state binding energy for the molecule has been determined. The atomic energy is usually calculated with an atomic parametric Hamiltonian that may be simulated with respect to atomic excitations.

In the simulation process several constraints may be imposed to minimize expression 22; for example: (a) The $H_{\text{pa}_i}^{XY}$ is defined at the equilibrium bond distance for each I state. (b) The total energy $E_{\text{pa}_i}^{XY}$ functional has to have a minimum at the equilibrium bond distance.

The above-mentioned strategy is perhaps one of the simplest where the two constraints imply that two parameters have to be adjusted per each different type of diatomic molecule. Another strategy may be to use several binding energies for the same type of bond in a selected group of molecules. Of course, this means the use of more parameters per bond or per type of atoms. The suggested schemes do not discard a direct simulation of energy or binding energy functionals with respect to accurate data only from theoretical calculations. For example, constraints may involve a close reproduction of the electronic energy at different internuclear distances (i.e., the matching of dissociation energy curves).

Although the theoretical aspects of simulating energy functionals and Hamiltonians is completely general, the particular examples proposed here, in the next section, differ from traditional ones (using a carefully chosen set of molecules and minimizing the residual between the observed and the calculated properties).^{14,28,29} In our case, a set of diatomic molecules is used (one for each type of bond), and different molecular electronic states are calculated, in order

Table 2. Equilibrium Bond Distances for C–C and C–H Bonds in CH₄, C₂H₂, C₂H₄, and C₂H₆ Molecules Using Different Functionals

distance	molecule			
	CH ₄	C ₂ H ₂	C ₂ H ₄	C ₂ H ₆
functional (A)				
C–C (Å)		1.2611	1.3681	1.5187
C–H (Å)	1.1039	1.0917	1.1021	1.1052
functional (B)				
C–C (Å)		1.2639	1.3790	1.5394
C–H (Å)	1.1036	1.0897	1.1014	1.1055
functional (C)				
C–C (Å)		1.2489	1.3093	1.5000
C–H (Å)	1.1020	1.0972	1.1026	1.0950
MINDO/3				
C–C (Å)		1.1961	1.3205	1.4870
C–H (Å)	1.1020	1.0707	1.0984	1.1102
experimental value				
C–C (Å)		1.203	1.337	1.536
C–H (Å)	1.094	1.060	1.086	1.091

^a See expressions given in Table 1.

to assure the parametrization for the ground state configuration, particularly for transition metals molecules. The reference data for molecular systems are essentially dissociation energies (binding energies) and equilibrium bond distances. In the case of binding energy, the parametrization is easily performed with respect to high-level *ab initio* results, instead of calculated thermochemical data. The use of several parametrization techniques such as genetic algorithm,^{1d} neural network, simulated annealing, etc. are not discarded; however, complications may appear due to electronic state changes during parametrization.

6. PARAMETERIZATION AND CALCULATION FOR A SET OF MOLECULES

In previous works¹² a comparative study of energy functional components of a parametric Hamiltonian (H_{pa}) (MINDO/3²¹) and the corresponding ones obtained from an analytical method was carried out. Results showed that important improvements of total, electronic, and core–core repulsion energies can be obtained by modifying the way of simulating electron repulsion integrals. Some modifications to the MINDO/3 Hamiltonian²¹ were proposed in order to test the effect of a better simulation of the energy functional components with respect to analytical values. The following changes were carried out: (a) The two-center integrals γ_{XY} were evaluated by interpolation of a database of integral average analytically calculated at different distances. (b) All one-center integrals were analytically evaluated. (c) An effective potential for core electrons was included as calculated in HONDO/8.³⁰ (d) Gaussian basis sets were used. (e) The core–core interaction includes a functional that, as it is explained in section 3, corresponds to correlation energy between electrons on different atoms.

In this work, we have used the above-mentioned Hamiltonian in order to study in more detail the parametrization procedure using simulation techniques, as mentioned in section 5. In addition, the transferability and the use of different functionals have been explored. Thus, a parametrization of diatomic molecules is carried out for different functionals of the electronic and core–core repulsion in a

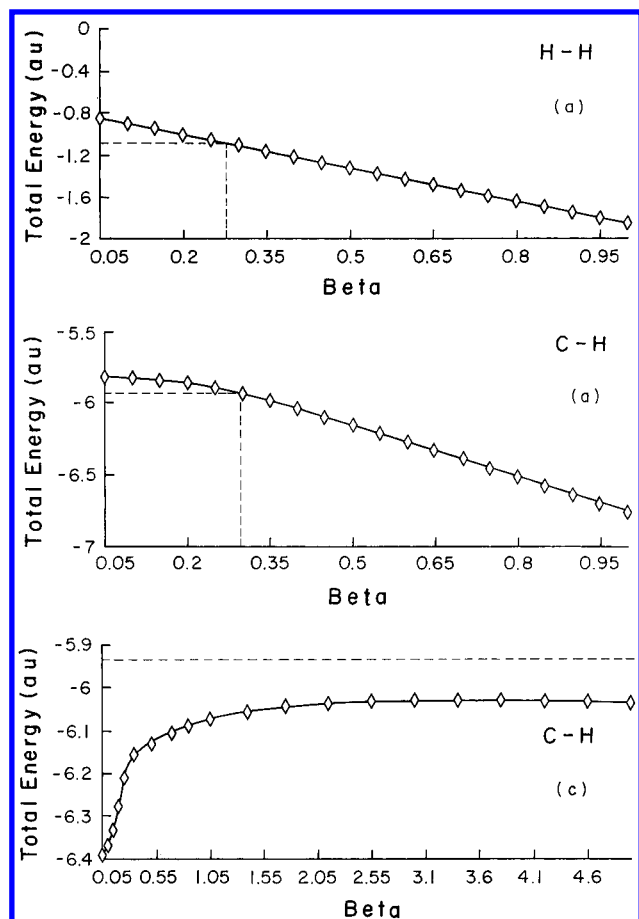


Figure 1. Variation of total energy vs β parameter with the condition of $\nabla E_t = 0$. (a) means that the $E_n = Z_X Z_Y ((ss', ss') + (1/R_{XY} - (ss', ss')) \alpha_{XY} e^{-R_{XY}})$ functional is used. (c) indicates that the $E_n = \alpha_{XY} Z_X Z_Y / R_{XY}$ functional is employed.

very simple way. For example, variation of the total energy (E_t) with the parameter β_{XY} (β_{XY} is used in the simulation of the two-center core-Hamiltonian, $H_{uv} = \beta_{XY} S_{uv} (I_u + I_v) / 2$) has been plotted for H-H and C-H; see Figure 1. In each curve, the total energy is calculated at a gradient equal to zero, using an accurate equilibrium bond distance obtained from the literature. It was found that E_t , under those constraints, in many cases is almost a linear function of β_{XY} . Therefore, a linear extrapolation procedure will be adequate to find α_{XY} and β_{XY} parameters. Note, however, that it is not always possible to find parameters (those depend on the type of functional used) that give correct binding energies and equilibrium bond distances, as shown in Figure 1c.

A preliminary test for evaluation of parameters using three different core-core functionals has been carried out employing the standard Mulliken approach. Results are shown in Table 1. Note that equilibrium bond distances are very close to experimental values (see total energy gradients). The binding energies are also in close agreement with the experimental data.

In order to evaluate the transferability of parameters to reproduce experimental findings, calculations of equilibrium bond distances for C-C and C-H bond distances of simple molecules are listed in Table 2 using different core-core functionals. Results show reasonable values, even though the parameters have been adjusted, with no respect to a set of molecules but with respect to the most simple molecules (diatomic). Note also that an optimal basis set is not

considered, because the one-center and two-center repulsion integrals come from an average of a STO-3G basis set.¹²

Parametrization for transition metals was also tested as shown in the last row of Table 1 using the Ni_2 molecular data. Note that a different core-core functional is used in which a new parameter $C_d = 1.03$ is employed. Calculations for a Ni_5 cluster in C_{4v} symmetry were performed for the best multiplicity, and a total energy of -172.6 kcal/mol was found, which is quite similar to that obtained with MINDO/SR method³¹ (-169.5 kcal/mol).

7. CONCLUSIONS

(a) The foundation of parametric Hamiltonians can be easily understood in terms of simulation techniques. Minimization of the distance between integral elements implies minimization of Hamiltonian components and therefore the optimization of the total energy functional.

(b) An energy functional based on the CI approach can be used as reference for simulation of parametric Hamiltonians. A parametric energy functional of dynamic correlation is proposed as a term that depends on the HF density matrix elements.

(c) Components of the matrix elements of the parametric Hamiltonian are represented in terms of an unknown basis set as functions or functionals. Therefore, the basis explicit set used gives only a qualitative representation of the electronic orbitals and is employed to built functionals such as the resonance integral term.

(d) A strategy of parametrization is proposed with respect to energies involved in bond formation of molecules and in excitations of atoms. The simulation using binding energy functionals from diatomic molecules is shown to be very simple to optimize parametric Hamiltonians.

(e) Calculations of parameters from diatomic molecules are straightforward, and the results presented in this work indicate that a reasonable transferability of parameters to polyatomic organic and metallic cluster can be obtained.

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