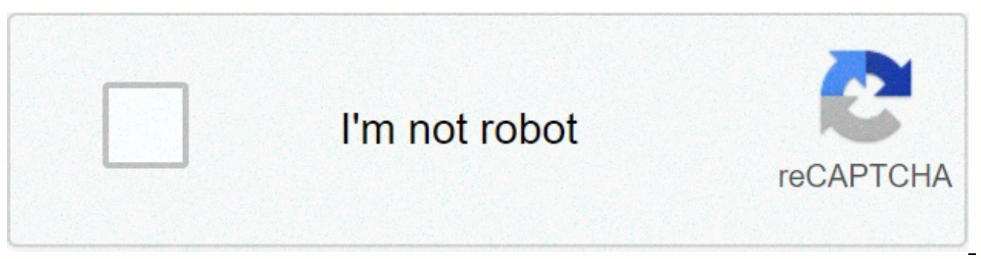
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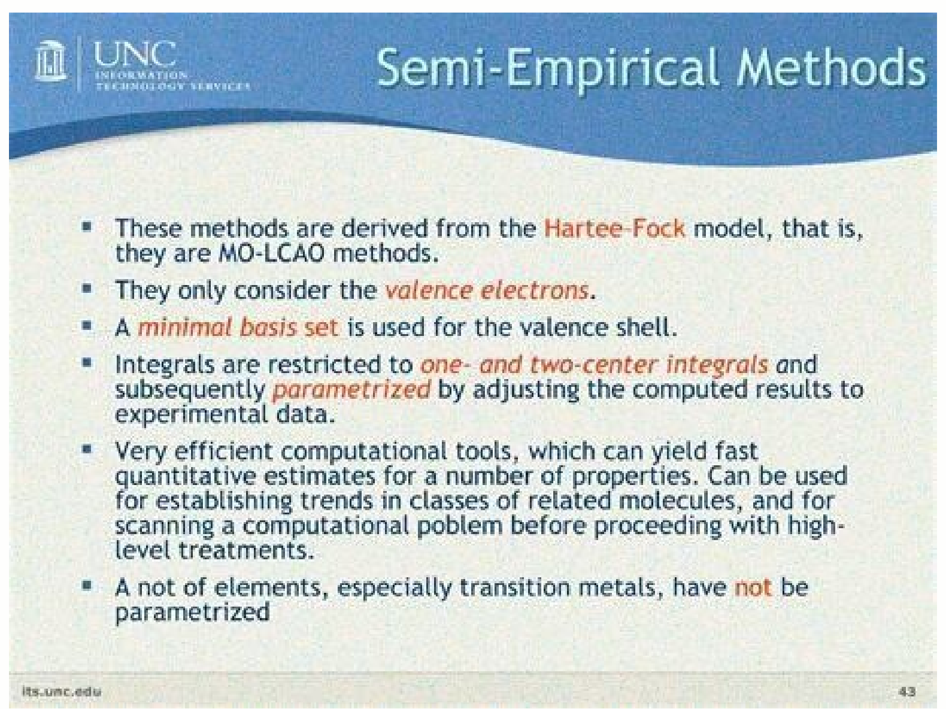
Semiempirical methods.

Semiempirical Methods are simplified versions of Hartree-Fock theory using empirical (= derived from experimental data) corrections in order to improve performance. These methods are usually referred to through acronyms encoding some of the underlying theoretical assumptions. The most frequently used methods (MNDO, AM1, PM3) are all based on the Neglect of Differential Diatomic Overlap (NDDO) integral approximation, while older methods use simpler integral schemes such as CNDO and INDO. All three approaches belong to the class of Zero Differential Overlap (ZDO) methods, in which all two-electron integrals involving two-center charge distributions are neglected. A number of additional approximations are made to speed up calculations (see below) and a number of parameterized corrections are made in order to correct for the approximate quantum mechanical model. How the parameterization is performed characterizes the particular semiempirical method. For MNDO, AM1, and PM3 the parameterization is performed such that the calculated energies are expressed as heats of formations instead of total energies (see earlier remarks on this difference).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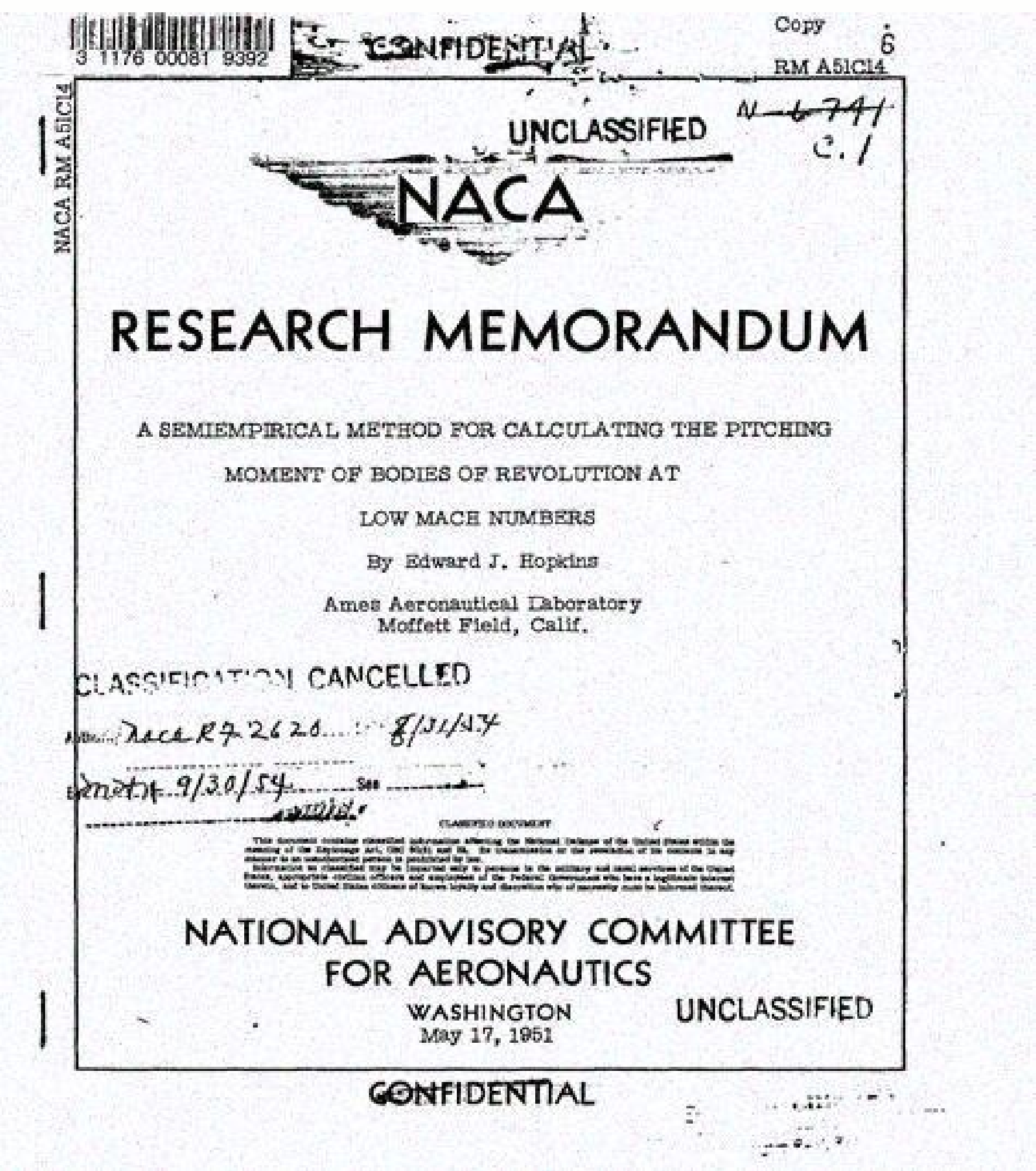
Semi-Empirical Methods

- These methods are derived from the Hartee-Fock model, that is, they are MO-LCAO methods.
- They only consider the *valence electrons*.
- A *minimal basis set* is used for the valence shell.
- Integrals are restricted to *one- and two-center integrals* and subsequently *parametrized* by adjusting the computed results to experimental data.
- Very efficient computational tools, which can yield fast quantitative estimates for a number of properties. Can be used for establishing trends in classes of related molecules, and for scanning a computational poblem before proceeding with high-level treatments.
- A not of elements, especially transition metals, have not be parametrized

In the following we will concentrate on the three methods available in Gaussian (MNDO, AM1, PM3). The first strategy used to reduce computational effort is to consider only valence electrons in the quantum mechanical treatment. This is immediately obvious when comparing Hartree-Fock with, for example, AM1 energy calculations on a molecule such as methanol: #P AM1 scf=tight AM1 energy of CH3OH (Cs) 0 1 C1 H2 1 r2 O3 1 r3 2 a3 H4 3 r4 1 a4 2 180.0 H5 1 r5 2 a5 3 d5 H6 1 r5 2 a5 3 -d5 r2=1.11900473 r3=1.41043172 r4=0.9641002 r5=1.11868093 a3=105.12806298 a4=107.16494018 a5=110.03331541 d5=119.51560095 Even though methanol CH3OH is composed of overall 6 nuclei and 18 electrons, only 14 of the electrons are treated explicitly. The electrons located in the 1s orbitals of oxygen and carbon are not considered explicitly, but combine with the nuclei to provide an effective core potential for the valence electrons: AM1 Standard basis: VSTO-3G (5D, 7F) . . 12 basis functions 36 primitive gaussians 7 alpha electrons 7 beta electrons nuclear repulsion energy 25.1935849033 Hartrees. HF/STO-3G Standard basis: STO-3G (5D, 7F) . . 14 basis functions 42 primitive gaussians 9 alpha electrons 9 beta electrons nuclear repulsion energy 40.2200678489 Hartrees. The basis sets used in semiempirical calculations are specially optimized minimal basis sets composed of Slater-type orbitals. As only valence electrons are considered and the core electrons are treated together with the nuclei as one effective core potential, it is clear that the simple point charge model used in Hartree-Fock theory to calculate the nuclear repulsion energies is inappropriate for semiempirical calculations. In order to compensate for some of the approximations made in calculating the attractive core-electron energies, the core-core potential used in NDDO methods goes beyond the use of a simple point charge model with reduced nuclear charges such as: EAB = Z'AZ'Be2/RAB with RAB being the internuclear separation and Z'A being the effective core charge including the nuclear charge and all core electrons. A general expression for calculation of the core-core repulsion energies between nuclei A and B at distance RAB in NDDO methods is: EAB = Z'AZ'B[1+ F(A) + F(B)] The core repulsion energy is here a function of both the electron-electron repulsion integral as well as atom-type dependent functions F(A) and F(B) which in turn depend on the internuclear separation RAB. Functions F(A) and F(B) have a relatively simple form in MNDO: including only one additional parameter. In order to improve some of the deficiencies of MNDO (especially those concerning hydrogen bonding), a slightly more complex function was chosen for AM1: The sum over additional exponentials inlcudes either three or four terms and introduces three new parameters KAi, LAi, and MAi for each element constituting the main difference (aside from the actual fitting procedure) between AM1 and MNDO. Which set of parameters is used in a given semiempirical calculation is specified in the Gaussian output file as: References: H: (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985) C: (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985) O: (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985) For some of the elements, the core repulsion functions F(A) for a given element depend on the interaction partner B. Taking the element boron as an example, there are four different sets of parameters describing the core of boron implying that Fboron is different in EBB, EBH, EBC, and EBX!! Please note that this functionality is not implemented in all programs, Gaussian being one of the problematic cases. It is therefore not possible to perform AM1 calculations on boron-containing compounds in Gaussian. Any attempt to do so anyway will lead to a calculation with mixed AM1 and MNDO parameters identified in the output file as follows: References: H: (AM1): M.J.S. DEWAR ET AL, J. AM. CHEM. SOC. 107 3902-3909 (1985) B: (MNDO): M.J.S. DEWAR, M.L. MCKEE, J. AM. CHEM. SOC., 99, 5231, (1977) Warning. AM1 has been requested, along with some elements for which only MNDO parameters are available. Such mixtures of methods are very risky and have not been fully tested. Indeed, these types of calculations are extremely unreliable and not worth doing under any circumstance. The performance of NDDO methods for a large number of molecular systems has been studied repeatedly and the mean signed and unsigned errors for the heat of formation (kJ/mol) in a set of 194 typical organic systems containing the elements C, H, N, and O has been collected in the following table: method MAD unsigned MAD signed MNDO47.7+20.1 AM130.1+10.9 PM318.4+0.9 The performance is much worse for all three methods in cases involving second-row elements such as S or P, the description of hypervalent compounds being particularly problematic. Another critical area of application concerns calculations of nitrogen-containing compounds. While the inversion barriers for trivalent nitrogen are usually too low with AM1, they are predicted to be too high with PM3.



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RESEARCH MEMORANDUM

A SEMIEMPIRICAL METHOD FOR CALCULATING THE PITCHING
MOMENT OF BODIES OF REVOLUTION AT
LOW MACH NUMBERS

By Edward J. Hopkins

Ames Aeronautical Laboratory
Moffett Field, Calif.

CLASSIFICATION CANCELLED

Naca R7 2626 8/31/54

9/30/54

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NATIONAL ADVISORY COMMITTEE
FOR AERONAUTICS
WASHINGTON
May 17, 1951

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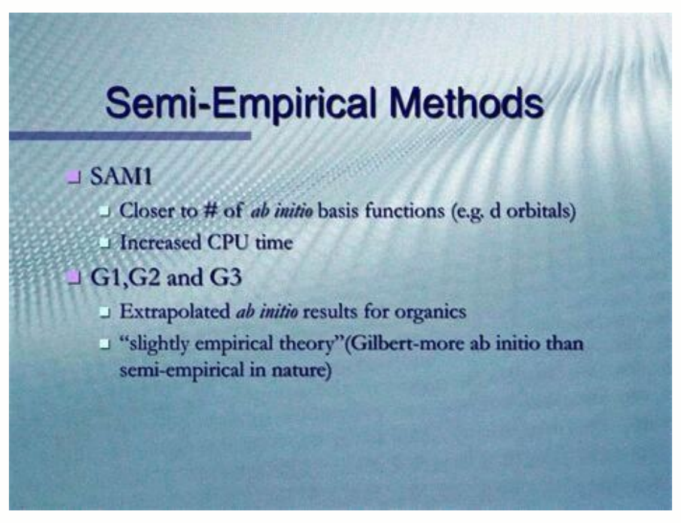
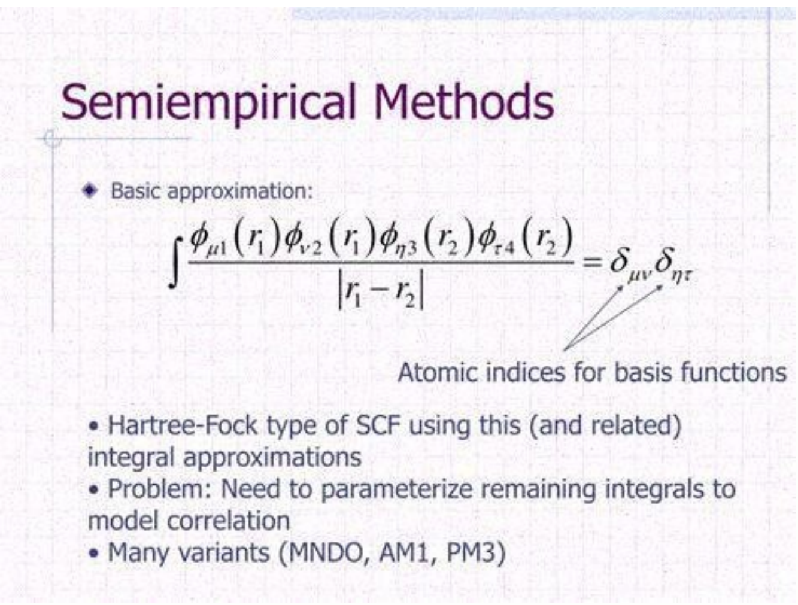
How the parameterization is performed characterizes the particular semiempirical method. For MNDO, AM1, and PM3 the parameterization is performed such that the calculated energies are expressed as heats of formations instead of total energies (see earlier remarks on this difference).
acronym full name underlying approximation Parameters Fitted-Parameters CNDO Complete Neglect of Differential OverlapCNDO - - INDO Intermediate Neglect of Differential OverlapINDO - - MINDO/3 Modified Intermediate Neglect of Differential Overlap, version 3INDO102 MNDO Modified Neglect of Differential OverlapNDDO105 AM1 Austin Model 1NDDO138 PM3 Parametric Model number 3NDDO1313 New versions of the NDDO methods have recently been developed that include d-Orbitals for second-row and higher elements (MNDO/d and PM3(tm)).



Semi-Empirical Methods

- SAM1
  - Closer to # of *ab initio* basis functions (e.g. d orbitals)
  - Increased CPU time
- G1,G2 and G3
  - Extrapolated *ab initio* results for organics
  - "slightly empirical theory"(Gilbert-more ab initio than semi-empirical in nature)

How the parameterization is performed characterizes the particular semiempirical method. For MNDO, AM1, and PM3 the parameterization is performed such that the calculated energies are expressed as heats of formations instead of total energies (see earlier remarks on this difference).



Semiempirical Methods

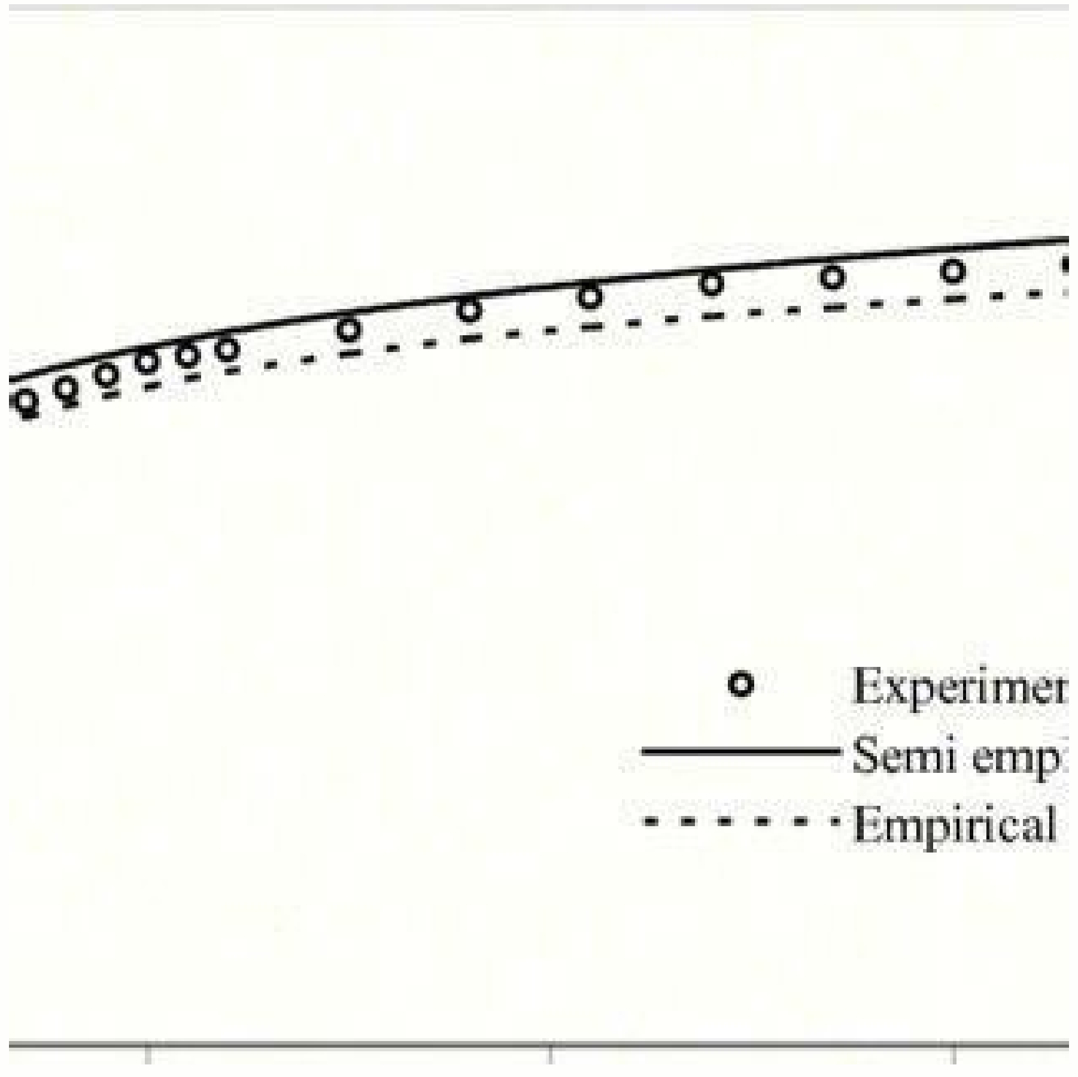
- Basic approximation:

$$\int \frac{\phi_{\mu 1}(r_1)\phi_{\nu 2}(r_1)\phi_{\eta 3}(r_2)\phi_{\tau 4}(r_2)}{|r_1 - r_2|} = \delta_{\mu\nu}\delta_{\eta\tau}$$

Atomic indices for basis functions

- Hartree-Fock type of SCF using this (and related) integral approximations
- Problem: Need to parameterize remaining integrals to model correlation
- Many variants (MNDO, AM1, PM3)

The most frequently used methods (MNDO, AM1, PM3) are all based on the Neglect of Differential Diatomic Overlap (NDDO) integral approximation, while older methods use simpler integral schemes such as CNDO and INDO. All three approaches belong to the class of Zero Differential Overlap (ZDO) methods, in which all two-electron integrals involving two-center charge distributions are neglected. A number of additional approximations are made to speed up calculations (see below) and a number of parameterized corrections are made in order to correct for the approximate quantum mechanical model. How the parameterization is performed characterizes the particular semiempirical method. For MNDO, AM1, and PM3 the parameterization is performed such that the calculated energies are expressed as heats of formations instead of total energies (see earlier remarks on this difference). acronym full name underlying approximation Parameters Fitted-Parameters CNDO Complete Neglect of Differential OverlapCNDO - - INDO Intermediate Neglect of Differential OverlapINDO - - MINDO/3 Modified Intermediate Neglect of Differential Overlap, version 3INDO102 MNDO Modified Neglect of Differential OverlapNDDO105 AM1 Austin Model 1NDDO138 PM3 Parametric Model number 3NDDO1313 New versions of the NDDO methods have recently been developed that include d-Orbitals for second-row and higher elements (MNDO/d and PM3(tm)). Also, a slightly extended and reparameterized version of PM3 termed PM5 has recently been made available in the program package MOPAC 2000.



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STEWART, J. COMP. CHEM. 10, 209 (1989). C: (PM3): J. J. P. STEWART, J. COMP. CHEM. 10, 209 (1989). N: (PM3): J. J. P. STEWART, J. COMP. CHEM. 10, 209 (1989). O: (PM3): J. J.

P. STEWART, J. COMP. CHEM. 10, 209 (1989). A reliable prediction of peptide conformations is, however, not possible even with these corrections. One important point to consider when comparing the performance of semiempirical calculations with other theoretical methods such as Hartree-Fock or DFT is that the former have been parameterized to include all thermochemical corrections to yield heat of formations at 300K, while the latter have not. Also, through parameterization with reference to experimental data, semiempirical methods *might* be expected to recover some part of electron correlation effects. This is, of course, only true for the ground state systems included in the parameterization procedure and not necessarily true for transition states or electronically excited states.

last changes: 12.12.2005, HZ questions & comments to: zipse@cup.uni-muenchen.de Semi-empirical methods modify Hartree-Fock calculations by introducing functions with empirical parameters. The method is highly demanding, especially for larger systems. This approximation is introduced on the basis of experimentation rather than the chemical grounds which parameterizes the two-electron integrals, making the computation faster. Another method to reduce the two-electron integral is the Zero Differential Overlap (ZDO) approximation. All modern semi-empirical methods are based on the Modified Neglect of Differential Overlap (MNDO) approach.

In this method, parameters are assigned for different atomic types and are fitted to reproduce properties such as heats of formation, geometrical variables, dipole moments, and first ionization energies. The parameterization was carried out separately for classes of compounds such as hydrocarbons, CHO systems, CHN systems, and so on. The latest versions of the MNDO method are referred to as AM1 and PM3. The setting up of the Hamiltonian system for semi-empirical methods has been included to facilitate computing. An exhaustive comparison of semi-empirical methods has been made. An application of the methods in various fields with specific examples has been added. A sufficient number of exercises are included.KeywordsThese keywords were added by machine and not by the authors. This process is experimental and the keywords may be updated as the learning algorithm improves. This is a preview of subscription content, log in via an institution. Unable to display preview. Download preview PDF. Bliznyuk AA, Voityuk (1989) Proton affinities of nucleic bases and their complexes. Zh Phys Khim 63:1227-1230CAS Google Scholar Fu H et al. (2004) A novel perchlorate-bridged tetranuclear zinc(II) structure with tris(2-aminoethyl)amine ligand.

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