

Volume 4

Q-S

Editor-in-Chief

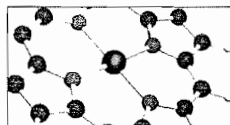
Paul von Ragué Schleyer

University of Georgia, Athens, USA,

Professor Emeritus

Universität Erlangen-Nürnberg, Erlangen, Germany

ENCYCLOPEDIA OF COMPUTATIONAL CHEMISTRY



JOHN WILEY & SONS

Chichester · New York · Weinheim · Brisbane · Singapore · Toronto

25. D. G. Oakenfull and D. E. Fenwick, *J. Phys. Chem.*, 1974, **78**, 1759-1763.
26. V. Gogonea and E. Osawa, *Supramol. Chem.*, 1994, **3**, 303-317.
27. J. P. M. Postma, H. J. C. Berendsen, and J. R. Haak, *Faraday Symp. Chem. Soc.*, 1982, **17**, 55-67.
28. W. L. Jorgensen, J. Chandrasekhar, J. D. Madura, R. W. Impey, and M. L. Klein, *J. Chem. Phys.*, 1983, **79**, 926-935.
29. (a) M. J. Mandell and H. Reiss, *J. Stat. Phys.*, 1975, **13**, 107-112; (b) R. M. C. Gonçalves, A. M. N. Simões, and J. J. Moura-Ramos, *J. Solution Chem.*, 1993, **22**, 507-517.
30. O. Sinanoglu, 'Molecular Associations in Biology', ed. B. Pullman. Academic Press, New York, 1968. p. 427-445.
31. O. Sinanoglu, *Theor. Chim. Acta*, 1974, **33**, 279-284.
32. M. H. Abraham and A. Nasehzadeh, *J. Chem. Soc. Faraday Trans. 1*, 1981, **77**, 321-340.
33. (a) C. B. Gogonea, 'MS Thesis', Toyohashi University of Technology, Toyohashi, 1996; (b) C. B. Gogonea, V. Gogonea, and E. Osawa, in 'Proc. Int. Chem. Conf. Pacific Basin Soc.', Honolulu, HI, 1995, pp. 17-22.
34. P. Claverie, 'Intermolecular Interactions: from Diatomics to Biomolecules', ed. B. Pullman, Wiley, Chichester, 1978.
35. V. Gogonea, 'PhD Thesis', Toyohashi University of Technology, Toyohashi, 1996.
36. (a) V. Gogonea, B. C. Gogonea, and E. Osawa, in 'Proc. Kyushu Int. Symp. on Physical Organic Chemistry KISPOC-VI', Fukuoka, Japan, 1995, pp. 328-333; (b) V. Gogonea and E. Osawa, *J. Comput. Chem.*, 1995, **16**, 817-842.
37. J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, 'Molecular Theory of Gases and Liquids', John Wiley, New York, 1964.
38. (a) P. Th. van Duijnen, A. H. Juffer, and H. Dijkman, *J. Mol. Struct. (Theochem)*, 1992, **260**, 195-205; (b) D. Rinaldi, B. J. Costa-Cabral, and J.-L. Rivail, *Chem. Phys. Lett.*, 1986, **125**, 495-499; (c) M. A. Aguilar and F. J. Olivares del Valle, *Chem. Phys.*, 1989, **138**, 327-336.
39. (a) M. J. Huron and P. Claverie, *J. Phys. Chem.*, 1974, **78**, 1862-1867; (b) J.-L. Rivail and D. Rinaldi, *Chem. Phys.*, 1976, **18**, 233-242; (c) O. Tapia, F. Sussman, and E. Poulain, *J. Theor. Biol.*, 1978, **71**, 49-72.
40. W. C. Still, A. Tempczyk, R. C. Hawley, and T. Hendrickson, *J. Am. Chem. Soc.*, 1990, **112**, 6127-6129.
41. C. J. Cramer and D. G. Truhlar, 'Reviews in Computational Chemistry', eds. K. B. Lipkowitz and D. B. Boyd, VCH, New York, 1995, Vol. 6, pp. 1-72.

Semiempirical Methods: Integrals and Scaling

James J. P. Stewart

Stewart Computational Chemistry, Colorado Springs, CO, USA

1	Introduction	2574
2	The Roothaan-Hall Equation	2574
3	MINDO/3 Semiempirical Approximation	2575
4	NDDO Semiempirical Approximation	2575
5	Advantages of the NDDO Formalism	2577
6	Limitations of NDDO Formalism	2577
7	Related Articles	2578
8	References	2578

1 INTRODUCTION

Modern semiempirical methods involve the generation of a self-consistent field. In this, the electron distribution is made a function of the kinetic and potential energy of the electrons. In part, the potential energy depends on the distribution of the electrons; that is the energy of the electrons is a function of the inter-electron interactions. In LCAO methods, these interactions are limited to two-electron interactions, as described by the Roothaan equations.¹

Because evaluation of the two-electron interaction energies is very difficult, the development of SCF methods has evolved into two branches, one of which, the *ab initio* methods, attempt the rigorous and nonempirical evaluation of these terms. The other branch, semiempirical methods, avoids even attempting the evaluation of the integrals involved; instead they are replaced with approximations.

The purpose of this article is to describe the two-electron approximations used in the NDDO² series of semiempirical methods, MNDO (see *MNDO*),³ AM1 (see *AMI*),⁴ and PM3 (see *PM3*),⁵ and to discuss the implications of these approximations on the ability of the resulting methods to model systems of chemical interest.

2 THE ROOTHAAN-HALL EQUATION

Semiempirical methods, like *ab initio* methods, define the elements of the Fock matrix, $F_{\mu\nu}$, using the Roothaan-Hall equation,^{1,6} as shown in equation (1),

$$F_{\mu\nu}^{\alpha} = H_{\mu\nu} + \sum_{\lambda} \sum_{\sigma} \left[P_{\lambda\sigma}^{\alpha+\beta} \langle \mu\nu | \lambda\sigma \rangle - P_{\lambda\sigma}^{\alpha} \langle \mu\lambda | \nu\sigma \rangle \right] \quad (1)$$

in which $H_{\mu\nu}$ is the one-electron Hamiltonian, $P_{\lambda\sigma}^{\alpha}$ is the density matrix, and $\langle \mu\nu | \lambda\sigma \rangle$ are the two-electron integrals over atomic orbitals, φ_{λ} , as shown in equation (2).

$$\langle \mu\nu | \lambda\sigma \rangle = \int_0^{\infty} \int_0^{\infty} \varphi_{\mu}^1 \varphi_{\nu}^1 \frac{1}{R_{12}} \varphi_{\lambda}^2 \varphi_{\sigma}^2 d\tau_1 d\tau_2 \quad (2)$$

For the purposes of the discussion to follow, the Roothaan equation in its spin-free form (equation 3) is more convenient to use.

$$F_{\mu\nu} = H_{\mu\nu} + \sum_{\lambda} \sum_{\sigma} \left[P_{\lambda\sigma} \langle \mu\nu | \lambda\sigma \rangle - \frac{1}{2} P_{\lambda\sigma} \langle \mu\lambda | \nu\sigma \rangle \right] \quad (3)$$

This equation is difficult to solve for several reasons. Most important, the evaluation of the two-electron integrals is extremely difficult. In *ab initio* methods, the atomic orbitals are approximated using a Gaussian series expansion. This allows the integrals to be evaluated to any desired level of confidence, but the computational effort is still great, and, for large systems, this approach is prohibitively slow. Nevertheless, such methods are capable of very high accuracy.

Semiempirical methods followed a different path. Instead of trying to solve the integrals, they are replaced by approximations. This resulted in the development of many closely related yet distinct methods, the more popular of which were CNDO,^{2,7,8} INDO,^{2,9} methods MINDO/3¹⁰ and SINDO,¹¹ the NDDO methods, and ZINDO. All these methods use a common approximation, that is, all two-electron three- and four-center integrals are set to zero. Because there are differences

between the various semiempirical methods, the following discussion will be restricted to the MINDO/3 and NDDO approximations. These illustrate the theory involved, that is, with only minor modifications, the ideas developed by the discussion of these methods can be applied to the other methods.

3 MINDO/3 SEMIEMPIRICAL APPROXIMATION

MINDO/3 was the first of the modern semiempirical methods. The main improvement over earlier methods was the use of molecular rather than atomic data in determining parameters. In this method, the two-electron integrals were partitioned into two distinct types: one-center integrals, those dependent on only the type of element involved; and two-center integrals, which depended on the types of atoms involved and on the interatomic separation.

3.1 One-center Integrals

In MINDO/3, the values of the one-center two-electron integrals were obtained from atomic spectra.¹² For atoms with an s-p basis set, there are six one-center two-electron integrals, as shown in Table 1. One of these integrals, however, is related to two others, as shown in equation (4); consequently there are only five independent one-center integrals.

$$H_{pp} = \frac{1}{2}(G_{pp} - G_{pp'}) \quad (4)$$

In performing semiempirical calculations, it is essential that this relationship be maintained; if it is not, then rotational invariance, an essential for any valid method, would not be maintained.

Because these quantities are atomic constants, they should not be regarded as being parameters.

3.2 Two-center Integrals

The approximation to the two-center two-electron integral used in MINDO/3 is that proposed by Dewar and Sabelli,¹³ and is shown in equation (5),

$$\gamma_{ab} = \langle \varphi_a \varphi_a | \varphi_b \varphi_b \rangle = \frac{c}{\sqrt{R_{ab}^2 + \frac{1}{4} \left(\frac{c}{\gamma_{aa}} + \frac{c}{\gamma_{bb}} \right)^2}} \quad (5)$$

in which expression c has the value 14.397, as indicated in equation (6).

$$c = \frac{e^2}{a_0} \quad (6)$$

Table 1 One-center Two-electron Integrals

Integral	Symbol
$\langle ss ss \rangle$	G_{ss}
$\langle ss pp \rangle$	G_{sp}
$\langle sp sp \rangle$	H_{sp}
$\langle pp pp \rangle$	G_{pp}
$\langle pp p'p' \rangle$	$G_{pp'}$
$\langle pp' pp' \rangle$	H_{pp}

The properties of this function are of interest. For very small R_{ab} , the function collapses to γ_{aa} . That is, the function correctly predicts the one-center two-electron energy. At very large distances, the function collapses to $1/R_{ab}$, which is the expected behavior for two point charges. At intermediate distances, the function is slightly less than that expected by the point-charge approximation.

3.3 Limitations of the γ_{ab} Approximation

This function depends on the properties of the two atoms involved, but does not differentiate between the various atomic orbitals involved. As a result, the electrostatic interactions of a p orbital are the same as those of an s orbital. While this keeps the method simple, it does reduce the flexibility of the method.

More importantly, the function contains no terms which can model the behavior of a lone pair: because all integrals of the type $\langle \varphi_\lambda \varphi_\sigma | \varphi_b \varphi_b \rangle$ in which λ is not the same as σ are zero, lone pairs, which involve s-p hybrid orbitals, cannot be represented. A consequence of this is that phenomena that depend on lone pair-charge or lone pair-lone pair interactions cannot be modeled. This situation cannot be rectified by an appropriate choice of parameter values - the model simply does not have the flexibility to allow such phenomena to be modeled.

4 NDDO SEMIEMPIRICAL APPROXIMATION

In 1977 the NDDO approximation³ was proposed. In this, many of the defects of MINDO/3 were corrected. In particular, the two-electron two-center integral approximation was changed to allow all integrals involving any two orbitals on one atom with any two orbitals on a second atom to be modeled. This increased the number of integrals dramatically. For each atom with an s-p basis set, there are 10 distinct pairs of atomic orbitals (Table 2). Therefore, for two dissimilar non-hydrogen atoms, there are a total of 100 different two-electron two-center integrals, where in MINDO/3 there had been only one.

The NDDO approximation for the new integrals can best be understood in terms of the point-charge expansion of the atomic orbital pairs. Examples of the four possible multipolar charge distributions are shown in Figure 1. The s-s charge distribution is spherically symmetric, and therefore can be represented by a single unit charge at the atom. A lone pair is represented by the s-p distribution. This has a net charge of zero, and behaves like a dipole centered on the atom. Each p-p pair behaves like the s-s pair, but is modified by the angular dependence of the orbital. Like the s-s distribution, the net charge is unity. Finally, the p-p' distribution corresponds to a simple quadrupole.

$$\langle \varphi_\mu \varphi_\nu | \varphi_\lambda \varphi_\sigma \rangle = \sum_i \sum_j \frac{c Q_i Q_j}{\sqrt{R_{ab}(ij)^2 + \frac{1}{4} \left(\frac{1}{d_{\mu\nu}} + \frac{1}{d_{\lambda\sigma}} \right)^2}} \quad (7)$$

Table 2 Atomic Orbital Pairs

ss			
sp _x	P _x P _x		
sp _y	P _x P _y	P _y P _y	
sp _z	P _x P _z	P _y P _z	P _z P _z

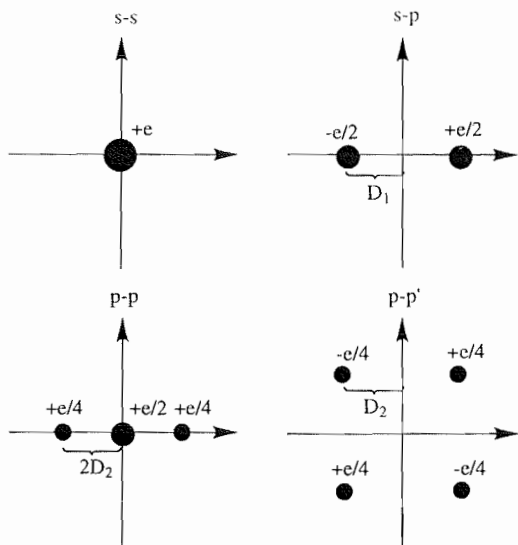


Figure 1 Point charge distributions for pairs of atomic orbitals

The general form of the approximation for the two-electron two-center integral is as shown in equation (7), in which $R_{ab}(ij)$ is the distance between point-charge Q_i on atom a and point charge Q_j on atom b, and the d quantities are functions of the atomic orbitals on the respective atoms.

To see how these quantities relate, consider the integral $\langle p_x p_x | s p_z \rangle$, involving two atoms, as shown schematically in Figure 2. The six distances $R_{ab}(ij)$ then represent the distances between each of the three point charges representing the $p_x p_x$ distribution and the two point charges representing the $s p_z$ distribution. In this approximation, the quantity D_1 is chosen so that the multipole moment due to the point charges reproduces that expected from the product of an s and p atomic orbital, and can be calculated from the orbital exponents using equation (8).

$$D_1 = \frac{2n+1}{\sqrt{3}} \frac{(4\xi_s \xi_p)^{n+\frac{1}{2}}}{(\xi_s + \xi_p)^{2n+2}} \quad (8)$$

A similar expression exists for D_2 , based on the p orbital exponents (equation 9).

$$D_2 = \sqrt{\frac{(2n+1)(2n+2)}{20\xi_p^2}} \quad (9)$$

Unfortunately, the definition of the quantities $d_{\lambda\sigma}$ is not so straightforward. In MINDO/3, the equivalent quantity was chosen so that the integral would collapse to G_{ss} as R_{ab} went to zero. While this is the same in the NDDO approximation

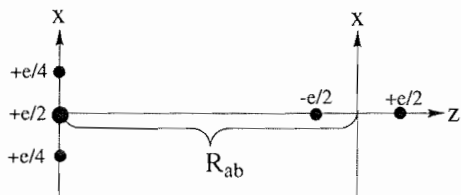


Figure 2 Two-electron integral $\langle p_x p_x | s p_z \rangle$

when the pair of orbitals are of type s (equation 10), the values when one or both orbitals are of type p is more complicated.

$$d_{\lambda\sigma} = \frac{G_{ss}}{c} \quad (10)$$

The nature of the problem when one or more p orbitals are involved can be seen when an attempt is made to evaluate the d_{sp} term. The interactions involved are shown in Figure 3. There are four of these: between the $+e/2$ and $-e/2$ point charges on atom a and the $+e/2$ and $-e/2$ point charges on atom b. At $R_{ab} = 0$, the equation for the integral is given in equation (11), in which the distance $R_{+a+a} = R_{-a-a} = 0$, and $R_{+a-a} = R_{-a+a} = 2D_1$.

$$H_{sp} = \frac{c}{4} \left(R_{+a+a} + \frac{1}{2} \left(\frac{1}{d_{sp}} + \frac{1}{d_{sp}} \right)^2 \right)^{-\frac{1}{2}} + \frac{c}{4} \left(R_{-a-a} + \frac{1}{2} \left(\frac{1}{d_{sp}} + \frac{1}{d_{sp}} \right)^2 \right)^{-\frac{1}{2}} - \frac{c}{4} \left(R_{+a-a} + \frac{1}{2} \left(\frac{1}{d_{sp}} + \frac{1}{d_{sp}} \right)^2 \right)^{-\frac{1}{2}} - \frac{c}{4} \left(R_{-a+a} + \frac{1}{2} \left(\frac{1}{d_{sp}} + \frac{1}{d_{sp}} \right)^2 \right)^{-\frac{1}{2}} \quad (11)$$

This expression can be re-arranged to give a quartic equation (equation 12).

$$D_1^2 c^2 d_{sp}^4 - 4H_{sp} D_1^2 c d_{sp}^3 + 4H_{sp}^2 D_1^2 d_{sp}^2 - H_{sp} c d_{sp} + H_{sp}^2 = 0 \quad (12)$$

No analytic solutions exist for such equations, but they can be solved by iterative means to any accuracy desired. Of the four solutions, only the real positive solution is meaningful. By inspection of the numerical values of the constants in equation (12), a starting estimate for the value of d_{sp} can be obtained (equation 13).

$$d'_{sp} \approx \left(\frac{2H_{sp}}{D_1^2 c} \right)^{\frac{1}{3}} \quad (13)$$

This estimate can be improved by use of the first differential (equation 14). After four or five iterations, the error in value of d_{sp} becomes vanishingly small.

$$d_{sp} = d'_{sp} - \frac{D_1^2 c^2 d_{sp}'^4 - 4H_{sp} D_1^2 c d_{sp}'^3 + 4H_{sp}^2 D_1^2 d_{sp}'^2 - H_{sp} c d_{sp}' + H_{sp}^2}{4D_1^2 c^2 d_{sp}'^3 - 12H_{sp} D_1^2 c d_{sp}'^2 + 8H_{sp}^2 D_1^2 d_{sp}' - H_{sp} c} \quad (14)$$

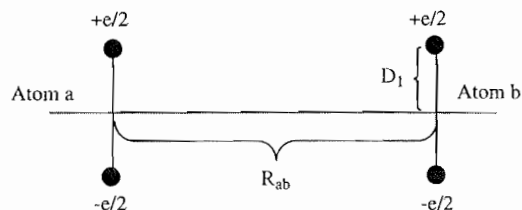


Figure 3 The $\langle sp | sp \rangle$ interaction

Table 3 Parameters for Carbon

Parameter	Value	Calc	Quantity	Value
G_{ss}	12.23	12.23	D_1	0.807466
G_{sp}	11.47	10.80	D_2	0.685158
G_{pp}	11.08	10.58	d_{ss}	0.449467
G_{p2}	9.84	10.00	d_{sp}	0.614947
H_{sp}	2.43	2.43	d_{pp}	0.668590
H_{pp}	0.62	0.62		

A similar, although slightly more complicated, expression can be derived for d_{pp} . At $R = 0$, the expression for d_{pp} is given by equation (15), in which the quantity D_2 is the distance from an axis to a point-charge, as seen in the p-p' interaction in Figure 1.

$$H_{pp} = \frac{c}{4} \left(d_{pp} - 2 \left(4D_2^2 + \frac{1}{d_{pp}^2} \right)^{-\frac{1}{2}} + \left(8D_2^2 + \frac{1}{d_{pp}^2} \right)^{-\frac{1}{2}} \right) \quad (15)$$

The expansion of this term to form a polynomial is tedious. Instead, the value of d_{pp} can be obtained directly using a starting value and iterating using equation (15) and its derivative, as shown in equation (16).

$$d_{pp} = d'_{pp} - \frac{\frac{c}{4} \left(d'_{pp} - 2 \left(4D_2^2 + \frac{1}{d_{pp}^2} \right)^{-\frac{1}{2}} + \left(8D_2^2 + \frac{1}{d_{pp}^2} \right)^{-\frac{1}{2}} \right) - H_{pp}}{\frac{c}{4} \left(1 - 2 \left(\frac{1}{d_{pp}^3} \left(4D_2^2 + \frac{1}{d_{pp}^2} \right) \right)^{-\frac{3}{2}} + \left(\frac{1}{d_{pp}^3} \left(8D_2^2 + \frac{1}{d_{pp}^2} \right) \right)^{-\frac{3}{2}} \right)} \quad (16)$$

in which the starting value of d_{sp} is given by equation (17).

$$d'_{pp} = 0.6 \left(\frac{H_{pp}}{D_2^2} \right)^{\frac{1}{3}} \quad (17)$$

Convergence is achieved in four to five iterations.

The advantage of using an approximation of this type is that no new parameters are introduced into the method. In the NDDO formalism, all two-center two-electron integrals are simple functions of the atomic orbitals, the one-center two-electron integrals, and the relative positions of the two atoms.

Both the one- and two-center integrals used in semiempirical methods are smaller than the equivalent values predicted from a first principles or analytical calculation (Table 3). This has been attributed¹⁴ to the implicit inclusion of correlation effects in the semiempirical values.

5 ADVANTAGES OF THE NDDO FORMALISM

A consequence of the increased sophistication of the NDDO method over that in MINDO/3 is that more subtle phenomena

can be modeled. Probably the most important specific improvement was that the electrostatic properties of lone pairs were now correctly modeled. The overall effect was that, for almost all types of systems, the new method gave much improved results.

6 LIMITATIONS OF NDDO FORMALISM

The NDDO formalism has very few limitations. Most chemical properties can be related to atomic or interatomic interactions. These interactions are accounted for in the NDDO formalism, so such phenomena can be modeled by this method. Very few, if any, phenomena can be related to triatomic or four-atom interactions. These are the types of interaction that are represented by *ab initio* calculations, and are ignored in semiempirical methods. Therefore the fact that these interactions are ignored does not provide prima facie evidence of a limitation in these methods.

There is one fault in the NDDO approximation to the two-electron integrals, a fault shared by the simpler approximation used in MINDO/3. This fault does not manifest itself in calculations on molecules or ions, or in calculations on polymers or layer systems, or even calculations on solid elements. Strangely enough it only shows up in calculations of three-dimensional solid-state compounds. To understand the nature of the problem, consider a solid compound of formula AB. If atom A carries a charge Q , then atom B carries a charge of $-Q$, and the potential generated at an atom A due to the two atoms in a distant unit cell will be of the form shown in equation (18).

$$V_A = \frac{Q_A}{\sqrt{R_{AA}^2 + \frac{1}{4} \left(\frac{1}{d_{AA}} + \frac{1}{d_{AA}} \right)^2}} - \frac{Q_A}{\sqrt{R_{AB}^2 + \frac{1}{4} \left(\frac{1}{d_{AA}} + \frac{1}{d_{BB}} \right)^2}} \quad (18)$$

Here the multipole expansion has been ignored: at large distances each atom behaves like a point charge. This potential has the form shown in equation (19),

$$V_A = Q_A \left((R_{AA}^2 + k_1^2)^{-\frac{1}{2}} - (R_{AA}^2 + k_2^2)^{-\frac{1}{2}} \right) \quad (19)$$

or, on expanding in a power series,

$$V_A \approx \frac{Q_A(k_2 - k_1)}{2R_{AA}^3} \quad (20)$$

The significance of this expression is that the potential generated at a point by two equidistant atoms carrying equal and opposite charges is not zero. The difference is, admittedly, small, and for discrete species, polymers and layer systems, the error is negligible. For solids, however, this is not the case.

For solids, the number of unit cells at any given distance from an atom rises as $4\pi R^2$, therefore the potential due to a shell of unit cells at distance R is as shown in equation (21).

$$V_A \approx 2\pi \frac{Q(k_2 - k_1)}{R} \quad (21)$$

This is still a negligible quantity. But the potential at an atom is due to unit cells at all possible radii, and that sum is infinite (equation 22).

$$V_A \approx \sum_R \frac{2\pi Q(k_2 - k_1)}{R}$$

$$V_A = 2\pi Q(k_2 - k_1) \sum_R \frac{1}{R}$$

$$V_A = \infty \quad (22)$$

The implication of this is that the calculated semiempirical potential experienced by an atom in a solid compound would be infinite. This is likely to hinder the development of a useful semiempirical solid state method.

7 RELATED ARTICLES

AM1; Integrals of Electron Repulsion; Integrals: Overlap; MNDO; MNDO/d; PM3.

8 REFERENCES

1. C. C. Roothaan, *J. Rev. Mod. Phys.*, 1951, **23**, 69-89.
2. J. A. Pople and D. L. Beveridge, 'Approximate Molecular Orbital Theory', McGraw-Hill, New York, 1970.
3. M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.*, 1977, **99**, 4899-4907.
4. M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, and J. J. P. Stewart, *J. Am. Chem. Soc.*, 1985, **107**, 3902-3909.
5. J. J. P. Stewart, *J. Comput. Chem.*, 1989, **10**, 209-220.
6. G. G. Hall, *Proc. R. Soc. London*, 1951, **A205**, 541-542.
7. J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1965, **43**, S136-S149.
8. J. A. Pople and G. A. Segal, *J. Chem. Phys.*, 1966, **44**, 3289-3296.
9. J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 1967, **47**, 2026-2033.
10. R. C. Bingham, M. J. S. Dewar, and D. H. Lo, *J. Am. Chem. Soc.*, 1975, **97**, 1285-1293.
11. D. N. Nanda and K. Jug, *Theor. Chim. Acta*, 1980, **57**, 95-106.
12. L. Oleari, L. DiSipio, and G. DeMichells, *Mol. Phys.*, 1966, **10**, 97-109.
13. M. J. S. Dewar and N. L. Sabelli, *J. Chem. Phys.*, 1962, **66**, 2310-2316.
14. M. J. S. Dewar and W. Thiel, *Theor. Chim. Acta*, 1977, **46**, 89-104.

Semiempirical Methods: Transition Metals

Andrew J. Holder

University of Missouri-Kansas City, Kansas City, MO, USA

Abbreviations

MNDO = modified neglect of differential overlap;
MNDO/d = modified neglect of differential overlap with d-functions.

1 DISCUSSION

Transition metal elements are a real test of the efficacy of quantum chemical theories. Primarily, this is because many (if not most) of these systems have unpaired electrons, i.e., are open shell. Open shell systems therefore require additional approximations beyond standard Hartree-Fock theory to make the calculations tractable computationally. These include the UHF (unrestricted Hartree-Fock) and configuration interaction (CI) approaches. Both approaches are computationally costly and have complicating considerations that make their general application more difficult and less straightforward. Also, it is often difficult to determine which spin state is the correct or natural one, and properties can vary substantially with differences in spin state.

A few semiempirical approaches are currently available that may allow treatment of transition metals with efficiency. Two of these fall in the INDO class of HF models. (INDO methods are usually more computationally efficient, though not as accurate, as those based on NDDO theories.) INDO/S¹ developed by Zerner et al. is included in the ZINDO² package and has been available for a number of years. It is very successful for the prediction of electronic spectra, for which it was carefully parameterized. However, INDO/S is not usually applied to compute more general properties such as optimized geometries or molecular energies, as it is not deemed to be reliable for these values.³ SINDO1⁴ from Jug et al. has recently been expanded to some transition metal elements and performs as expected within the limited INDO theory used. Again, results are somewhat erratic and the method does not appear to treat open-shell systems with a great deal of success.

There are currently four NDDO methods for transition metals, only three of which have found some acceptance and use. SAM1,⁵ MNDO/d,⁶ and PM3(tm)⁷ are all implemented in commercial software packages (AMPAC,⁸ Unichem,⁹ and Spartan¹⁰ respectively) that are commonly available. Filatov et al. have also developed a method they call NDDO/MC,¹¹ which was published in 1992. While the three more accepted methods are intended to be general models predicting a wide range of chemical properties as the previous Dewar-style methods have done, NDDO/MC was aimed at reproducing geometries and binding energies, at which it performs relatively well. It was thus not directly parameterized to compute such items as heats of formation and electronic properties. Values of this type are needed for the study of reactions, an area in which semiempirical methods have traditionally been used the most extensively. NDDO/MC will find utility in certain circumstances, but will probably not become a general purpose method.

The MNDO/d method from Walter Thiel et al. was also introduced in 1992. This method still utilizes a modified point-charge model (multipole expansion as in AM1 and PM3) for computing the two-center two-electron integrals (TERIs). MNDO/d is essentially layered onto the older (1977) MNDO model for the elements where $Z < 11$. Heavier elements were then re-parameterized utilizing an expanded version of

1 Discussion	2578
2 Related Articles	2579
3 References	2579