ONE-ELECTRON PROPERTIES OF SIMULATED
NON-EMPIRICAL WAVEFUNCTIONS

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SUMMARY

One-Electron Properties of Simulated Non-Empirical Wavefunctions.


An approximate, but non-empirical, SCF LCAO-MO scheme for
single-determinantal wavefunctions is developed. The formulation of
this approach, Simulated Non-Empirical, or SNE, is shown to be
intermediate between the NDDO method and a complete ab initio treat-
ment.

The CNDO and NDDO schemes are discussed with regard to
their invariance to rotation and hybridisation using matrix formulations.
From the Mulliken and Ruedenberg approximations to bicentric orbital
products in a Slater orbital basis, a direct relationship is established
with the CNDO and NDDO methods in a basis of Löwdin orthonormalised
orbitals. Expansion of second-order correction terms vindicates
previously observed trends in repulsion integral values and serves a
warning that errors are likely to arise in the CNDO and NDDO formalisms
from failure to allow for integral modification on change of basis.

With the Ruedenberg approximation, a particularly simple
transformation may be effected from the set of coulomb integrals in a
Slater orbital basis to the full set of two-electron integrals in a
Löwdin basis. The SNE scheme is defined in terms of this transformation,
with truncation of the integral list to an effective NDDO set. One-
electron integrals are evaluated exactly, or may be approximated by
Ruedenberg expansion where appropriate. Care must be exercised with
Schmidt orthogonalisation outside a valence orbital basis.

The SNE scheme proves computationally economical, and some
of the programming features which contribute to this favourable
situation are outlined. Not least in this context is the method of
integral evaluation, based on a modified C-function route, and the
general features, as well as specific contributions to the evaluation
of auxiliary functions, are reviewed.

Calculations on the molecular systems H₂O and NH₃ use the
SNE scheme in two variants, whereby three-centre nuclear attraction
integrals may be evaluated exactly, or approximated. As well, both
minimal and valence orbital bases are employed. Since energy integrals
are approximated in the SNE scheme, total energy is discounted as a
criterion for optimisation of orbital exponents. Instead, experimental
one-electron properties are taken as standards, and extensive
calculations are undertaken to obtain, in each case, a set of orbital
exponents which enable reproduction of those properties. Further
calculations on H₂CO employ a minimal basis and exact nuclear attraction
integrals.

All exponent optimisations are successful in that the
required match with experimental properties could be achieved to a
satisfactory degree. As a consequence, no one variant or basis set
size can be recommended as superior. Experimental error limits are
sufficiently broad in most instances to preclude ultimate refinement
to a unique exponent set. The functional relationships between
exponents and expectation values are remarkably similar for many
operators, and this fairly general characteristic also inhibits
refinement to a unique set.

From a critical examination of one-electron properties for
representative optimised wavefunctions, it is apparent that there
exists no consistent correlation, either among the various approaches,
or in comparison with ab initio wavefunctions. Electron density maps
are in support, for, while total densities are remarkably alike, marked
differences occur with partitioning to molecular orbital contributions.

Inclusion of higher excited configurations, in a configura-
tion interaction calculation on formaldehyde, has a deleterious effect
on dipole moment, and, by inference, on other optimised one-electron
property expectation values. Excitation energies are in reasonable
accord with observed spectral transitions.