

ZINDO-MN: An Enhanced version of ZINDO Including the INDO/S2 Parameterization, the CM2 Class IV Charge Model, and the SM5.42R and VEM Solvation Models

Manual

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Contents

Reference	3
Abstract	3
Executive summary	4
Capabilities added to ZINDO in ZINDO-MN and references for methods	4
INDO/S2	4
CM2 partial atomic charges	5
SM5.42R/INDO/S and SM5.42R/INDO/S2 free energy calculations	5
VEM calculations of the electrostatic part of solvatochromic shifts	5
Theory of vertical excitation energy in liquid solution	6
A note on the VEM model and the ZINDO-MN code	9
A note on notation and models	11
Usage	12
Keywords in \$SRCRFIN	12
Input and output examples	14
Example 1: CM2/INDO/S dipole moment of acetone	14
Example 2: CM2/INDO/S2 dipole moment and excitation energy of the $n \rightarrow \pi^*$ excitation of acetone in the gas phase	16
Example 3: SM5.42R/INDO/S2 calculation of the ground state of acetone in aqueous solution	17
Example 4: VEM/INDO/S2 calculation of the first excited state of acetone in aqueous solution	17
Example 5: VEM/INDO/S2 calculation of acetone with one explicit water molecule in aqueous solution	18
Example 6: SM5.42R/INDO/S2 calculation of acetone in isobutanol (JSCRF=2).	19
Example 7: SM5.42R/INDO/S2 calculation of acetone in isobutanol (JSCRF=1).	20
Example 8: VEM/INDO/S2 calculation of the first excited state of coumarin 153 in dimethyl sulfoxide	21
Installation and running	22
Testing	24
Platforms	25
Special notes	25
SCF schemes	25
The VEM model	25
Availability of QM/MM in ZINDO-MN	26
Documentation	26
Revision history of ZINDO-MN	26

Reference

Users of ZINDO-MN should give the following reference:

M. C. Zerner, J. E. Ridley, A. D. Bacon, W. D. Edwards, J. D. Head, J. McKelvey, J. C. Cuberson, P. Knappe, M. G. Cory, B. Weiner, J. D. Baker, W. A. Parkinson, D. Kannis, J. Yu, N. Roesch, M. Kotzian, T. Tamm, M. M. Karelson, X. Zheng, G. Pearl, A. Broo, K. Albert, J. M. Cullen, J. Li, G. D. Hawkins, J. D. Thompson, C. P. Kelly, D. A. Liotard, A. V. Marenich, C. J. Cramer, and D. G. Truhlar, ZINDO-MN, version 2011, Quantum Theory Project, University of Florida, Gainesville, and Department of Chemistry, University of Minnesota, Minneapolis, 2011.

Abstract

The current version of ZINDO-MN adds INDO/S2 parameters, improved charges, and solvation modeling to a 1999 version of the ZINDO package. The gas-phase parts of ZINDO-MN calculations are based on the original INDO/S method or a modified version called INDO/S2, in which the oxygen parameters have been readjusted. The ZINDO-MN package includes the original ZINDO code plus new code for adding new capabilities and enhancements to ZINDO. The ZINDO-MN code includes the CM2 model for calculating class IV charges in the gas-phase or as part of a liquid phase solution calculation, the SM5.42R solvation model with INDO/S and INDO/S2 parameterizations for modeling equilibrium free energies of solvation of electronic ground states, and the VEM/INDO/S and VEM/INDO/S2 electrostatic models for calculating nonequilibrium free energies for modeling solvatochromic effects on electronically excited states and spectroscopy. The VEM model replaces the older VEM42 model.

One of the critical features in the SM5.42R solvation model and the new vertical electrostatic model is that the Class IV charge model, Charge Model 2 (CM2), is used in the calculation of atomic partial charges in both ground and excited states; this allows the

user to calculate improved charges in both the gas phase and liquid solutions. The user can employ the liquid phase charges in solvation models to calculate free energies of solvation of ground states. Class IV liquid phase charges can also be used in a two-response time theory to calculate the electrostatic part of the solvatochromic shifts, i.e., the electrostatic part of spectral shifts due to solvation effects, for vertically excited states by the VEM model.

In summary, ZINDO has been enhanced to include a new parameterization of INDO/S, two new parameterizations of the CM2 class IV charge model, two new parameterizations of the SM5.42R solvation model, in particular SM5.42R/INDO/S and SM5.42R/INDO/S2, and a new vertical electrostatic model, VEM. These models have been developed at the intermediate-neglect-of-differential-overlap-for-spectroscopy (INDO/S) level with INDO/S and INDO/S2 parameterizations. They have been implemented in an extended package called ZINDO-MN.

Executive summary

Capabilities added to ZINDO in ZINDO-MN and references for methods

ZINDO-MN adds the following capabilities to ZINDO:

INDO/S2

A new parameterization of the INDO/S model, called INDO/S2, has been added to ZINDO. The new model involves readjusting two oxygen parameters so as to reproduce better the first excitation energies for molecules containing carbonyl groups. The INDO/S2 model is described in J. Li, B. Williams, C. J. Cramer, and D. G. Truhlar, *J. Chem. Phys.* 110 (1999) 724-733.

CM2 partial atomic charges

The CM2 class IV model has been parameterized for INDO/S and INDO/S2, and these methods have been added to ZINDO. The CM2 model is described in J. Li, T. Zhu, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. A* 102 (1998) 1820-1831, and the parameterization for INDO/S and INDO/S2 is described in J. Li, B. Williams, C. J. Cramer, and D. G. Truhlar, *J. Chem. Phys.* 110 (1999) 724-733. The CM2 model allows one to calculate class IV charges (and hence dipole moments and electrostatic potentials) by a mapping of charges obtained by Löwdin population analysis. (At the INDO level, Löwdin charges reduce to zero-overlap Mulliken charges, which are in turn sometimes called Coulson charges). Using ZINDO-MN and standard ZINDO methods for ground and excited states, one can calculate gas-phase CM2 partial charges from INDO/S and INDO/S2 calculations. One can also calculate liquid phase CM2 charges for equilibrium solvated ground states and liquid phase charges for (nonequilibrium) nascent vertically excited states using the INDO/S or INDO/S2 parameterizations.

SM5.42R/INDO/S and SM5.42R/INDO/S2 free energy calculations

The SM5.42R/INDO/S and SM5.42R/INDO/S2 parameterizations of the SM5.42R solvation model are used to calculate equilibrium free energies of ground states, as described in J. Li, T. Zhu, C. J. Cramer, and D. G. Truhlar, *J. Phys. Chem. A* 104 (2000) 2178-2182. SM5.42R calculations have two components: a self-consistent reaction field (SCRF) calculation based on the generalized Born approximation and CM2 charges, and a first-solvation-shell calculation based on the exposed van der Waals surface area of each atom and a set of geometry-dependent atomic surface tensions.

VEM calculations of the electrostatic part of solvatochromic shifts

The program contains the VEM vertical excitation SM5.42R/INDO/S and SM5.42R/INDO/S2 modules to calculate the electrostatic part of the solvatochromic shift for vertical excitation in liquid solution. The theory is based on a two-response-time

treatment of absorption. The reaction field is obtained from the CM2 charges of both the ground and the excited state using a two-response-time theory and the generalized Born model. The calculations account for the part of the solvatochromic shift that is due to electrostatic effects of the liquid solvent. It is possible to parameterize first-solvation-shell effects to add to these electrostatic calculations to produce full SM5.42R calculations of solvatochromic shifts, but this has not been done yet. The results of two-response-time calculations carried out without surface tensions are called VEM/INDO/S or VEM/INDO/S2 (where VEM denotes vertical electrostatic model). The reference for VEM42 is J. Li, C. J. Cramer, and D. G. Truhlar, *Int. J. Quantum Chem.* 77 (2000) 264-280. Two updates to the original VEM42 algorithm have been made recently, resulting in the VEM model; these modifications are described in the section of this manual titled “A note on the VEM model and the ZINDO-MN code” as well as in the following manuscript: A. V. Marenich, C. J. Cramer, D. G. Truhlar, C. A. Guido, B. Mennucci, G. Scalmani, and M. J. Frisch, “Practical computational methods for electronic excitation in solution: Vertical excitation model,” *Chem. Sci.* 2 (2011) 2143-2161. This article introduces a unified treatment of solvatochromic shifts in liquid-phase absorption spectra within a self-consistent state-specific vertical excitation model called VEM. The VEM model can be used to calculate vertical excitation energies in solution within the generalized Born approximation using the CM2 partial atomic charges and the INDO/S2 electronic structure method.

Theory of vertical excitation energy in liquid solution

Expression for vertical excitation energy in liquid solution

The vertical excitation energy in solution is calculated as

$$\begin{aligned}\Delta E &= (\overline{\overline{E}}^g + \overline{\overline{G}}_P) - (\overline{\overline{E}}^g + \overline{\overline{G}}_P) \\ &= (\overline{\overline{E}}^g - \overline{\overline{E}}^g) - (\overline{\overline{G}}_P - \overline{\overline{G}}_P)\end{aligned}\tag{1}$$

where $\overline{\overline{E}}^g$ is the expectation value of the gas-phase Hamiltonian of the solvated wave function of an excited state, and $\overline{\overline{E}}^g$ is the expectation value of the gas-phase

Hamiltonian of the solvated wave function of the ground state. $\bar{\bar{G}}_P$ and \bar{G}_P are polarization free energies for the excited and ground states, respectively. In the VEM model, the difference of the polarization free energy between the excited and ground states is given by

$$\bar{\bar{G}}_P - \bar{G}_P = -C \sum_{k,k'} (\bar{\bar{q}}_k - \bar{q}_k) \bar{q}_{k'} \gamma_{kk'} - \frac{1}{2} B \sum_{k,k'} (\bar{\bar{q}}_k \bar{\bar{q}}_{k'} - \bar{q}_k \bar{q}_{k'}) \gamma_{kk'} \quad (2)$$

where

$$B = \left(1 - \frac{1}{\epsilon_{opt}}\right) \quad (3)$$

$$C = \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon}\right) \quad (4)$$

Reaction field for excited states in liquid solution

In liquid solution, the electronic wave function of ground states can be obtained by solving an SCRF equation based on the GB model, i.e.

$$F^S \bar{\Phi}_i = \epsilon_i^S \bar{\Phi}_i \quad (5)$$

where F^S is the solvated Fock operator, $\bar{\Phi}_i$ is a solvated molecular orbital, and ϵ_i is the orbital energy. F^S can be expressed as follows

$$F_{\mu\nu}^S = F_{\mu\nu}^g + R_{\mu\nu} \quad (6)$$

where R is the reaction field and its matrix elements can be obtained by

$$R_{\mu\nu} = -\delta_{\mu\nu} V_{k_\mu} \quad (7)$$

where V_k can be regarded as the electrostatic potential induced by the polarized solvent medium at each atomic center k . For ground states, the potential can be obtained, according to generalized Born model, as following

$$V_k(\bar{\Psi}) = -\sum_{k'} \left(1 - \frac{1}{\epsilon}\right) \bar{q}_{k'} \gamma_{kk'} \quad (8)$$

For vertical excited states, the reaction field can be obtained by a two-response-time theory:

$$\begin{aligned} V_k(\bar{\Psi}, \bar{\bar{\Psi}}) &= -\sum_{k'} \left[\left(1 - \frac{1}{\epsilon_{opt}}\right) \bar{q}_{k'} \gamma_{kk'} + \left(\frac{1}{\epsilon_{opt}} - \frac{1}{\epsilon}\right) \bar{q}_{k'} \gamma_{kk'} \right] \\ &= -B \sum_{k'} \bar{q}_{k'} \gamma_{kk'} - C \sum_{k'} \bar{q}_{k'} \gamma_{kk'} \end{aligned} \quad (9)$$

The matrix elements of one-electron Hamiltonian, therefore, take the following form:

$$h_{\mu\nu}^s = h_{\mu\nu}^g - \delta_{\mu\nu} V_{k_\mu}(\bar{\Psi}, \bar{\bar{\Psi}}) \quad (10)$$

INDO/S-CIS calculation of excited states in liquid solution

In the INDO/S-CIS formalism, we can expand the excited-state wave function in the following form

$$\bar{\bar{\Psi}} = \sum_i C_i \bar{\Psi}_i \quad (11)$$

where $\{\bar{\Psi}_i\}$ are configurations of single excitations of the reference wave function of the solvated ground state, and $\{C_i\}$ is a eigenvector of the CI matrix, whose elements are given

$$H_{ij} = \langle \bar{\Psi}_i | H^g + R | \bar{\Psi}_j \rangle \quad (12)$$

In order to evaluate the CI matrix elements, the reaction field R for the excited state is obtained from Eqs. (9) and (10), and is added to the gas-phase one-electron Hamiltonian. ZINDO CI subroutines are called subsequently (i.e. whenever the one-electron Hamiltonian is involved in ZINDO-MN CI subroutines, it will be replaced by the modified one with inclusion of the reaction field R. In practice, this can be easily done by just modifying the one-electron Hamiltonian before calling CI subroutines. The modification with reaction field of the excited states is performed immediately after the SCF procedure is completed. A point here is that, Eq. (9) involves the CM2 charges of the excited state, which are not available before the CI is performed. This problem is solved by introducing an iterative procedure, i.e., using the CM2 charges of the excited state from a previous CI

calculation. For the first iteration, one uses ground state CM2 charges as an approximation.

What one obtains directly from a CIS calculation in solution with the ZINDO-MN program are the eigenvalues (i.e., \bar{E}) of the solvated CI matrix. The eigenvalue \bar{E} is actually the expectation value of the solvated Hamiltonian with the expectation value of the reference configuration (the ground state) set to zero, i.e.,

$$\bar{E} = \langle \bar{\Psi} | H^g + R | \bar{\Psi} \rangle - \langle \bar{\Psi} | H^g + R | \bar{\Psi} \rangle \quad (13)$$

Therefore,

$$\begin{aligned} \bar{E}^g - \bar{E}^g &= \langle \bar{\Psi} | H^g | \bar{\Psi} \rangle - \langle \bar{\Psi} | H^g | \bar{\Psi} \rangle \\ &= \bar{E} - \langle \bar{\Psi} | R | \bar{\Psi} \rangle + \langle \bar{\Psi} | R | \bar{\Psi} \rangle \\ &= \bar{E} - Tr(\bar{D}R) + Tr(\bar{D}R) \end{aligned} \quad (14)$$

where \bar{D} and \bar{D} are the one-electron density matrices of the excited-state and ground-state wave functions, which are available in ZINDO-MN CI subroutines. Finally, in the VEM model, we have

$$\begin{aligned} \Delta E &= \bar{E} - Tr(\bar{D}R) + Tr(\bar{D}R) - C \sum_k \sum_k (\bar{q}_k - \bar{q}_k) \bar{q}_k \gamma_{kk'} \\ &\quad - \frac{1}{2} B \sum_k \sum_k (\bar{q}_k \bar{q}_k' - \bar{q}_k \bar{q}_k') \gamma_{kk'} \end{aligned} \quad (15)$$

A note on the VEM model and the ZINDO-MN code

The VEM algorithm used in the current version of the ZINDO-MN program and described in this document is identical to the VEM42 model developed by J. Li, C. J. Cramer, and D. G. Truhlar [Int. J. Quantum Chem. 77 (2000) 264-280] and implemented in earlier versions of ZINDO-MN, except for two modifications.

First, the last term (“cross-term”) of equation 20 in the aforementioned paper has been removed. This term was inconsistent within the VEM42 formulation and is therefore not

present in the VEM method presented here. The inconsistency is related to an inconsistent partitioning of slow and fast polarization charges. The two commonly used partitioning schemes are called Partition I (sometimes called the Marcus partition) and Partition II (sometimes called the Pekar partition). Partitions I and II are defined here according to notations of J. Tomasi, B. Mennucci, R. Cammi [Chem. Rev. 105 (2005) 2999-3093]. The older formulation, called the VEM42 model, was developed based on equation 35 of Aguilar et al's paper [J. Chem. Phys. 98 (1993) 7375-7384] that was derived within the apparent surface charge model and Partition I's definition of slow and fast polarization surface charges. To translate this equation into its generalized Born form, the older VEM42 model uses Partition II, instead of Partition I. In fact, when applied consistently, both partitions lead to the same expression for the nonequilibrium excited-state polarization free energy, i.e., to equation 20 in the paper of Li et al [Int. J. Quantum Chem. 77 (2000) 264-280] without the last term ("cross-term"). All the equations in this manual, in particular, Eq. (2) and Eq. (15), correspond to the corrected VEM model.

Second, the older versions of ZINDO-MN by default calculated the CIS matrix that includes the H_{0n} elements where "0" refers to the Slater determinant of the ground state in solution and "n" refers to the n th excited-state determinant generated by single excitations from orbitals occupied in the ground-state state to virtual orbitals. In the present study, we do the CIS in the basis of singly excited basis states rather than in the basis of the ground state plus singly excited states, forcing the wave function of the resulting vertically excited state of interest in solution to be orthogonal to the ground-state wave function. We do this by working in the orbital basis of the ground-state SCRF calculation and deleting the first row and column of the CIS matrix corresponding to the H_{0n} elements even though the matrix need not be block diagonal. The VEM model is now defined to always involve the removal of the liquid-phase ground state from the expansion of the liquid-phase excited-state wave function. This change would not make a difference if the configurations were constructed from SCF orbitals obtained with the same Hamiltonian as used to calculate the CIS matrix or if the excited state has a different symmetry than the ground state.

A note on notation and models

The SM5.42R model is a special case of the SM5.42 model in which the solute is “rigid” (R), i.e., the solute is fixed at a gas-phase geometry. In SM5.42, in contrast, the calculations are based on geometries optimized in liquid solution or on molecular dynamics calculations in liquid solution. The SM5.42 and SM5.42R models have been parameterized in the rigid mode, but the same parameters are used for calculations in non-rigid modes, i.e., without the R. Parameters for SM5.42 and SM5.42R calculations are available for several ab initio Hartree-Fock calculations, density functional theory, hybrid Hartree-Fock-density-functional theory, and also in semiempirical molecular orbital theory in four parameterizations, AM1, PM3, INDO/S, and INDO/S2. In most of these cases, analytic liquid phase gradients are available in one or another computer program, allowing convenient SM5.42 calculations as well as SM5.42R calculations. However, the ZINDO-MN package does not support analytic gradients in the liquid phase. Hence, the ZINDO-MN package is intended for SM5.42R calculations with the INDO/S and INDO/S2 parameterizations.

All SM5.42 and SM5.42R calculations are based on SM5 functional forms for atomic surface tensions and class IV point charges obtained by charge model 2 (CM2). CM2 models are available for ab initio Hartree-Fock calculations, density functional theory, hybrid Hartree-Fock-density-functional theory, AM1, PM3, INDO/S, and INDO/S2. However, the INDO/S and INDO/S2 parameterizations are unique in that the CM2 model was explicitly parameterized for electronically excited states as well as ground states. The ZINDO-MN package can perform CM2 calculations for both ground and excited states in both the gas phase and liquid solution.

In all SM5.42 and SM5.42R models, the solute and solvent (including both electronic and nuclear-motion degrees of freedom of the solvent) polarize self-consistently by a self-consistent reaction field (SCRF) calculation. In SM5.42R calculations, only the

electronic polarization of the solute is included explicitly, where SM5.42 calculations also include geometric (i.e., nuclear) polarization of the solute. The polarization of the solvent is described according to dielectric continuum theory and is therefore technically described as “electric polarization”.

The VEM model implemented here uses CM2 charges in the ground and excited states in liquid solution to calculate absorption spectra. The excited states are treated according to a vertical excitation model in which the electronic modes of solvent polarization adjust self-consistently to the excited state while the nuclear-motion modes of solvent polarization are still in equilibrium with the ground state (corresponding to vertical excitation).

Usage

In order to use the capabilities added to ZINDO outlined in the executive summary, the user must specify `ISCRF 50` (notice that the space is required) in the `$CNTRL` section of the input file. The details of a particular calculation involving these newly added features are specified with keywords in the `$SCRFIN` section of the input file. A summary of available ZINDO-MN keywords follows. Note that the keywords of the original ZINDO code are described elsewhere, see for example, the ZINDO manual at http://www.ccl.net/cca/documents/ZINDO_manual. The ZINDO-MN package also includes several useful documents regarding the use of the original components of ZINDO. These documents are located in the *manuals* directory of the ZINDO-MN distribution package.

Keywords in `$SRCRFIN`

JSCRFF: Controls the type of SCF calculation to be performed.

- `JSCRFF=0` invokes a gas-phase calculation of CM2 charges and dipole moment (this is the default).

- JSCRF=1 invokes a gas-phase and liquid phase calculation of CM2 charges and dipole moment and a calculation of the free energy of solvation using SCF scheme I (see the section entitled *SCF schemes* for more details).
- JSCRF=2 invokes a gas-phase and liquid phase calculation of CM2 charges and dipole moment and a calculation of the free energy of solvation using SCF scheme II (see the section entitled *SCF schemes* for more details). When calculating excited states, we recommend using this scheme.

INDOS: Controls the parameters used for the CM2 charge model, the SM5.42R solvation model, and the VEM vertical excitation model for calculating the electrostatic part of solvatochromic shifts in solution.

- INDOS=1 uses INDO/S parameters (this is the default for historical reasons).
- INDOS=2 uses INDO/S2 parameters (these are more accurate).

ISTA: Determines the excited state with which to iterate the reaction field. Note that only this root of the CI matrix will be physically meaningful. Other eigenvalues and eigenvectors of the CI matrix are not self-consistent and are therefore non-physical. The default value is ISTA=2 (i.e., the second CI root and the first excited state).

DIELEC: The value of the dielectric constant of the solvent. The default value is 78.3, which is the dielectric constant for water.

IAQU: Determines the type of solvent:

- IAQU=1 specifies that the solvent is water (this is the default).
- IAQU=0 specifies that a general organic solvent will be used. The specific solvent desired is specified by the user in ZINDO-MN by inputting several solvent descriptors in \$SCRFIN, in particular, SOLN, SOLA, SOLB, SOLG, SOLC, SOLH.

SOLN: The value of the index of refraction at optical frequencies at 293K, n . The default value is 1.333, which is the value for water.

SOLA: The value of Abraham's hydrogen bond acidity parameter, $\sum \alpha_2^H$. The default value is SOLA=0.0.

SOLB: The value of Abraham's hydrogen bond basicity parameter, $\sum \beta_2^H$. The default value is SOLA=0.0.

SOLG: The value of the macroscopic surface tension, $\gamma = \gamma_m / \gamma^o$, where γ^o equals 1 cal·mol⁻¹·Å⁻² (note that 1 dyne/cm = 1.43932 cal·mol⁻¹·Å⁻²). The default value is SOLG=0.0.

SOLC: The value of the aromaticity parameter, ϕ : the fraction of non-hydrogenic solvent atoms that are aromatic carbon atoms. The default value is SOLC=0.0.

SOLH: The value of the electronegative halogenicity parameter, Ψ : the fraction of non-hydrogenic solvent atoms that are halogens. The default value is SOLH=0.0.

Solvent parameters for many common organic solvents are tabulated in the *Minnesota Solvent Descriptor Database*, the latest version of which is available at:

<http://comp.chem.umn.edu/solvation>.

Input and output examples

This section gives explicit examples of how to use ZINDO-MN, plus critical sections of test output. See a directory called *examples* inside the ZINDO-MN distribution package.

Example 1: CM2/INDO/S dipole moment of acetone

Input

```
$TITLEI
acetone: CM2/INDO/S for ground and the first excited states. HF/MIDI!
geometry is used.
$END
$CONTRL
```

```

SCFTYP RHF RUNTYP CI ENTTYP COORD
UNITS ANGS INTTYP 1 IAPX 3 ISCRF 50
$END
$DATAIN
      .0000      .0000      .0000 8
      .0000      .0000      1.1992 6
      1.2918      .0000      1.9981 6
     -1.2918      .0000      1.9981 6
      2.1296      .0000      1.3116 1
     -2.1296      .0000      1.3116 1
      1.3489      .8782      2.6394 1
     -1.3489      .8782      2.6394 1
      1.3489     -.8782      2.6394 1
     -1.3489     -.8782      2.6394 1
$END
$CIINPU
  2  1  15  1  0  0  0  1  10  1  10
-60000.000 0.000000
  0  1  2  3  4
  1  12  12
 21  3  12  13  22
$END
$SCRFIN
$END

```

Note: In this example, we have 24 valence electrons and 22 molecular orbitals including 12 doubly occupied and 10 virtual orbitals. The CIS matrix is constructed using the occupied orbitals 3–12 and the virtual orbitals 12–22.

Output

Gas-phase dipole moment (Debye)

	X	Y	Z	Total
CM2	0.0000	0.0000	3.0406	3.0406
ZDO	0.0000	0.0000	2.9505	2.9505

```

## STATE      2
ENERGY ABOVE GRD STATE =  0.134639 h =  29549.8 CM-1

```

CM2 CHARGES AFTER MAPPING

ATOMIC #	CM2 CHARGE
8	-0.0589
6	-0.1992
6	0.0648
6	0.0648
1	0.0260
1	0.0260
1	0.0192
1	0.0192
1	0.0192
1	0.0192

DIPCM2 (DEBYE) X,Y,Z 0.000 0.000 1.395

CM2 DIPOLE (DEBYE) OF THE 2TH STATE 1.395

Example 2: CM2/INDO/S2 dipole moment and excitation energy of the $n \rightarrow \pi^*$ excitation of acetone in the gas phase

Input

```

$TITLEI
acetone, CM2/INDO/S2, HF/MIDI! geometry, gas-phase
$END
$CONTRL
SCFTYP RHF RUNTYP CI ENTTYP COORD
UNITS ANGS INTTYP 1 IAPX 3 ISCRF 50
$END

$DATAIN
      .0000      .0000      .0000 8
      .0000      .0000      1.1992 6
      1.2918      .0000      1.9981 6
     -1.2918      .0000      1.9981 6
      2.1296      .0000      1.3116 1
     -2.1296      .0000      1.3116 1
      1.3489      .8782      2.6394 1
     -1.3489      .8782      2.6394 1
      1.3489     -.8782      2.6394 1
     -1.3489     -.8782      2.6394 1
$END
$CIINPU
  2   1  15   1   0   0   0   1  10   1  10
-60000.000  0.000000
  0   1   2   3   4
  1  12  12
 21   3  12  13  22
$END
$SCRFIN
  INDOS=2
$END

```

Note: See a note in Example 1

Output

```

Gas-phase dipole moment (Debye)
-----
      X           Y           Z       Total
CM2      0.0000    0.0000    3.0521    3.0521
ZDO      0.0000    0.0000    3.1617    3.1617
-----

## STATE      2
ENERGY ABOVE GRD STATE = 0.151439 h = 33237.1 CM-1

CM2 CHARGES AFTER MAPPING
ATOMIC #           CM2 CHARGE
-----
  8                -0.1355
  6                -0.1660
  6                 0.0837
  6                 0.0837
  1                 0.0277
  1                 0.0277
  1                 0.0197
  1                 0.0197
  1                 0.0197
  1                 0.0197

DIPCM2 (DEBYE) X,Y,Z  0.000  0.000  1.997

CM2 DIPOLE (DEBYE) OF THE 2TH STATE 1.997

```


Example 3: SM5.42R/INDO/S2 calculation of the ground state of acetone in aqueous solution

Input

```

$titleI
acetone
$end
$control
SCFTYP RHF RUNTYP ENERGY ENTYP COORD
UNITS ANGS INTTYP 1 IAPX 3 ISCRF 50
$end
$DATAIN
      .0000      .0000      .0000 8
      .0000      .0000      1.1992 6
      1.2918      .0000      1.9981 6
     -1.2918      .0000      1.9981 6
      2.1296      .0000      1.3116 1
     -2.1296      .0000      1.3116 1
      1.3489      .8782      2.6394 1
     -1.3489      .8782      2.6394 1
      1.3489     -.8782      2.6394 1
     -1.3489     -.8782      2.6394 1
$end
$SCRFIN
  JSCRF=2  INDOS=2  DIELEC=78.3  IAQU=1
$end

```

Output

Solution dipole moment (Debye)

```

-----
              X           Y           Z           Total
CM2          0.0000      0.0000      3.8909      3.8909
ZDO          0.0000      0.0000      3.9490      3.9490

```

```

(1) EINDOS(G): GAS-PHASE ENERGY          -34.332859283 a.u.
(2) EINDOS(S): SOLUTE ENERGY            -34.331053019 a.u.
(3) (2)-(1): DISTORTION ENERGY           1.133 kcal/mol
(4) G_P: POLARIZATION FREE ENERGY        -6.499 kcal/mol
(5) DeltaG_EP= EHF(S) - EHF(G) + G_P      -5.366 kcal/mol
(6) G_CDS: CAVITY-DISPERSION-STRUCTURE    0.972 kcal/mol

```

```

Free energy of solvation:
DeltaG_S = (5) + (6)                      -4.393 kcal/mol

```

```

Energy of solute:
E_solute = EHF(G) + DeltaG_S              -34.339860261 a.u.

```

Example 4: VEM/INDO/S2 calculation of the first excited state of acetone in aqueous solution

Input

```

$titleI
VEM calc example4 with DIELEC=78.4 and SOLN=1.34164
$end
$control
SCFTYP RHF RUNTYP CI ENTYP COORD ITMAX 99 IPRINT -1
UNITS ANGS INTTYP 1 IAPX 3 ISCRF 50
$end
$DATAIN
0.000000      0.000000      1.393231 8
0.000000      0.000000      0.175962 6
0.000000      1.277595     -0.607353 6

```

```

0.000000    -1.277595    -0.607353  6
0.000000    2.138501    0.056265  1
0.000000   -2.138501    0.056265  1
0.877264    1.305459   -1.256477  1
0.877264   -1.305459   -1.256477  1
-0.877264    1.305459   -1.256477  1
-0.877264   -1.305459   -1.256477  1
$END
$SCIINPU
  2   1  10   1   0   0   0   1  10   1  10
-60000.000  0.000000
  0   1   2   3   4
  1  12  12
 21   1  12  13  22
$END
$SCRFIN
JSCRFF=2 ICSAVE=1 INDOS=2 ISTA=2 IAQU=1 DIELEC=78.4 SOLN=1.34164
$END

```

Note: Solvation calculations using the VEM model require a few iterations. During each iteration, an intermediate file fort.75 is generated for the purpose of holding CM2 charges for the ground state and excited states. This file is used as part of input for the next iteration. Our experience shows that three iterations are usually sufficient to give fully converged results. In this example, we have 24 valence electrons and 22 molecular orbitals including 12 doubly occupied and 10 virtual orbitals. The CIS matrix is constructed using the occupied orbitals 1–12 and the virtual orbitals 12–22.

Output

```

EXCITATION ENERGY IN SOLUTION
-----
ENGY (CM-1)  1      0.0  2  33935.7  3  65125.9  4  74782.4  5  83197.7
W(NM)        1      0.00  2   294.67  3   153.55  4   133.72  5   120.20
EV           1  0.000000  2  4.207496  3  8.074582  4  9.271837  5 10.315205
OSC          1  0.000000  2  0.000000  3  0.042117  4  0.011405  5  0.005348

```

Example 5: VEM/INDO/S2 calculation of acetone with one explicit water molecule in aqueous solution.

Input

```

$TITLEI
VEM calc example5 with DIELEC=78.4 and SOLN=1.34164
$END
$CONTRL
SCFTYP RHF RUNTYP CI ENTTPY COORD ITMAX 99 IPRINT -1
UNITS ANGS INTTYP 1 IAPX 3 ISCRF 50
$END
$DATAIN
.0000    .0000    .0000  8
.0000    .0000    1.1992  6
1.2918    .0000    1.9981  6
-1.2918    .0000    1.9981  6
2.1296    .0000    1.3116  1
-2.1296    .0000    1.3116  1
1.3489    .8782    2.6394  1
-1.3489    .8782    2.6394  1
1.3489   -0.8782    2.6394  1
-1.3489   -0.8782    2.6394  1

```

```

0.0000      0.0000      -1.7000  1
0.0000      0.0000      -2.6600  8
0.0000     -0.9439      -2.8773  1
$END
$CIINPU
  2      1      10      1      0      0      0      1      10      1      10
-60000.000  0.000000
  0      1      2      3      4
  1     16     16
 21      1     16     17     28
$END
$SCRFIN
JSCRFF=2 ICSAVE=1 INDOS=2 ISTA=2 IAQU=1 DIELEC=78.4 SOLN=1.34164
$END

```

Note: In this example, we have 32 valence electrons and 28 molecular orbitals including 16 doubly occupied and 12 virtual orbitals. The CIS matrix is constructed using the occupied orbitals 1–16 and the virtual orbitals 17–28.

Output

Solution dipole moment (Debye)

```

-----
          X          Y          Z      Total
CM2      0.0000    -1.4564     5.7387    5.9206
ZDO      0.0000    -0.8804     5.4167    5.4877

```

```

(1) EINDOS(G): GAS-PHASE ENERGY          -49.323350481 a.u.
(2) EINDOS(S): SOLUTE ENERGY            -49.321943949 a.u.
(3) (2)-(1): DISTORTION ENERGY           0.883 kcal/mol
(4) G_P: POLARIZATION FREE ENERGY        -9.303 kcal/mol
(5) DeltaG_EP= EHF(S) - EHF(G) + G_P     -8.420 kcal/mol
(6) G_CDS: CAVITY-DISPERSION-STRUCTURE   -0.191 kcal/mol

```

```

Free energy of solvation:
DeltaG_S = (5) + (6)                      -8.611 kcal/mol

```

```

Energy of solute:
E_solute = EHF(G) + DeltaG_S              -49.337072403 a.u.

```

EXCITATION ENERGY IN SOLUTION

```

-----
ENGY(CM-1)  1      0.0  2   34571.8  3   65038.0  4   75080.6  5   82928.2
W(NM)       1      0.00  2    289.25  3    153.76  4    133.19  5    120.59
EV          1  0.000000  2  4.286353  3  8.063684  4  9.308813  5 10.281790
OSC         1  0.000000  2  0.000000  3  0.052024  4  0.018922  5  0.000501

```

Example 6: SM5.42R/INDO/S2 calculation of acetone in isobutanol (JSCRFF=2).

Input

```

$TITLEI
pyridine in isobutanol
$END
$CONTRL
SCFTYP RHF RUNTYP ENERGY ENTTYP COORD
UNITS ANGS INTTYP 1 IAPX 3 ISCRF 50
$END
$DATAIN
      1.32450      0.00000      0.00000  6
      0.61890      1.18650      0.00000  6
      0.61890     -1.18650      0.00000  6
     -0.76210      1.13500      0.00000  6
     -0.76210     -1.13500      0.00000  6

```

```

-1.45650      0.00000      0.00000  7
 1.12560      2.13450      0.00000  1
 1.12560     -2.13450      0.00000  1
-1.34630      2.03880      0.00000  1
-1.34630     -2.03880      0.00000  1
 2.40050      0.00000      0.00000  1
$END
$SCRFIN
JSCRF=2  INDOS=2  SOLN=1.40  SOLA=0.37  SOLB=0.48  SOLG=32.4  DIELEC=16.78  IAQU=0
$END

```

Output

Solution dipole moment (Debye)

```

-----
              X           Y           Z           Total
CM2          2.7073      0.0000      0.0000      2.7073
ZDO          2.1055      0.0000      0.0000      2.1055

```

```

(1) EINDOS(G): GAS-PHASE ENERGY          -39.891678870 a.u.
(2) EINDOS(S): SOLUTE ENERGY            -39.890943709 a.u.
(3) (2)-(1):  DISTORTION ENERGY          0.461 kcal/mol
(4) G_P:      POLARIZATION FREE ENERGY   -2.471 kcal/mol
(5) DeltaG_EP= EHF(S) - EHF(G) + G_P     -2.009 kcal/mol
(6) G_CDS:    CAVITY-DISPERSION-STRUCTURE -4.053 kcal/mol

```

```

Free energy of solvation:
DeltaG_S = (5) + (6)                      -6.062 kcal/mol

```

```

Energy of solute:
E_solute = EHF(G) + DeltaG_S              -39.901339171 a.u.

```

Example 7: SM5.42R/INDO/S2 calculation of acetone in isobutanol (JSCR=1).

Input

```

$TITLEI
pyridine in isobutanol
$END
$CONTRL
SCFTYP RHF  RUNTYP ENERGY  ENTYP COORD
UNITS ANGS  INTTYP 1  IAPX 3  ISCRF 50
$END
$DATAIN
 1.32450      0.00000      0.00000  6
 0.61890      1.18650      0.00000  6
 0.61890     -1.18650      0.00000  6
-0.76210      1.13500      0.00000  6
-0.76210     -1.13500      0.00000  6
-1.45650      0.00000      0.00000  7
 1.12560      2.13450      0.00000  1
 1.12560     -2.13450      0.00000  1
-1.34630      2.03880      0.00000  1
-1.34630     -2.03880      0.00000  1
 2.40050      0.00000      0.00000  1
$END
$SCRFIN
JSCR=1  INDOS=2  SOLN=1.40  SOLA=0.37  SOLB=0.48  SOLG=32.4  DIELEC=16.78  IAQU=0
$END

```

Output

Solution dipole moment (Debye)

```

-----
              X           Y           Z           Total
CM2          2.7053      0.0000      0.0000      2.7053
ZDO          2.1030      0.0000      0.0000      2.1030

```

```

(1) EINDOS(G): GAS-PHASE ENERGY          -39.891678870 a.u.
(2) EINDOS(S): SOLUTE ENERGY            -39.890950996 a.u.
(3) (2)-(1):  DISTORTION ENERGY          0.457 kcal/mol

```

```

(4) G_P:          POLARIZATION FREE ENERGY          -2.466 kcal/mol
(5) DeltaG_EP=   EHF(S) - EHF(G) + G_P             -2.010 kcal/mol
(6) G_CDS:       CAVITY-DISPERSION-STRUCTURE       -4.053 kcal/mol

```

```

Free energy of solvation:
DeltaG_S = (5) + (6)                               -6.062 kcal/mol

```

```

Energy of solute:
E_solute = EHF(G) + DeltaG_S                       -39.901339639 a.u.

```

Example 8: VEM/INDO/S2 calculation of the first excited state of coumarin 153 in dimethyl sulfoxide

Input

```

$TITLEI
VEM calc example8 with DIELEC=46.8 and SOLN=1.41421
$END
$CONTRL
SCFTYP RHF RUNTYP CI ENTTYP COORD ITMAX 99 IPRINT -1
UNITS ANGS INTTYP 1 IAPX 3 ISCRF 50
$END
$DATAIN
-0.932545      -0.142648      -0.019826 6
-0.192092      1.047529      -0.028939 6
1.194176      1.083706      -0.037462 6
1.896500      -0.144949      -0.052061 6
1.164982      -1.374108      -0.061215 6
-0.208425      -1.349014      -0.031380 6
1.915221      2.410873      -0.025465 6
3.999420      1.078798      -0.295675 6
3.355662      2.240608      0.440785 6
4.009706      -1.396643      -0.221820 6
3.302278      -2.556706      0.456246 6
1.900123      -2.692549      -0.121715 6
1.324587      -3.454038      0.408438 1
3.875380      -3.472232      0.300755 1
1.900921      2.843012      -1.032152 1
-0.735053      -2.296717      -0.028965 1
3.925534      3.153098      0.258185 1
3.263813      -0.154843      -0.041285 7
4.031736      1.285076      -1.374929 1
5.024033      0.925047      0.045284 1
3.381948      2.036347      1.514944 1
1.382363      3.110618      0.620347 1
5.000616      -1.244749      0.209807 1
4.140616      -1.608710      -1.292327 1
3.251294      -2.368084      1.532687 1
1.975853      -3.016774      -1.165683 1
-2.362895      -0.017048      0.001065 6
-2.970764      1.185591      0.008348 6
-2.184603      2.409123      -0.007443 6
-3.203955      -1.266969      0.013047 6
-2.971375      -2.021708      -1.071279 9
-2.934892      -2.028248      1.084087 9
-4.512554      -1.006089      0.036013 9
-4.044853      1.302516      0.024316 1
-0.822136      2.262026      -0.029201 8
-2.628989      3.525517      -0.004555 8
$END
$CIINPU
  2   1   10   1   0   0   0   1   10   1   10
-60000.000  0.000000
  0   1   2   3   4
  1  58  58
  21  1  58  59 102
$END
$SCRFIN
JSCRFF=2 ICSAVE=1 INDOS=2 ISTA=2 IAQU=1 DIELEC=46.8 SOLN=1.41421

```

\$END

Note: In this example, we have 116 valence electrons and 102 molecular orbitals including 58 doubly occupied and 44 virtual orbitals. The CIS matrix is constructed using the occupied orbitals 1–58 and the virtual orbitals 59–102.

Output

```

EXCITATION ENERGY IN SOLUTION
-----
ENGY (CM-1)  1      0.0  2  27230.7  3  29690.0  4  34837.1  5  35922.8
W (NM)       1      0.00  2   367.23  3   336.81  4   287.05  5   278.38
EV           1  0.000000  2  3.376177  3  3.681092  4  4.319256  5  4.453856
OSC          1  0.000000  2  0.509753  3  0.003784  4  0.144410  5  0.073151

```

Installation and running

The current version of ZINDO-MN is distributed as a compressed tar file called *zindomn-v2011.tar.gz*. This file should be placed in the directory in which the user wishes to install the program, and then the following commands need to be issued:

```

gunzip zindomn_v2011.tar.gz
tar -xvf zindomn_v2011.tar

```

The installation instructions for installing ZINDO-MN are as follows:

- 1) `cd zindomn-v2011`
- 2) Depending on your platform and compiler, copy *makefile.x* to *Makefile* where *x* is *ibm* (for XL Fortran, AIX IBM), *gfortran* (for gfortran, Linux), *ifort* (for Intel Fortran, Linux)
- 3) `cd util`
- 4) Depending on your platform and compiler, copy *sysdep.x* to *sysdep.f* where *x* is *ibm* (for XL Fortran, AIX IBM), *gfortran* (for gfortran, Linux), *ifort* (for Intel Fortran, Linux)
- 5) `cd ../`
- 6) `make depend`
- 7) `make`

The *zindomn* binary should appear in the working directory.

The syntax for running the *zindomn* binary is

```
./zindomn < input > output
```

Replace *input* and *output* with the name of input and output files, respectively.

The *zindomn-v2011.tar.gz* distribution contains binaries *zindomn_aix*, *zindomn_ifort*, and *zindomn_gfort* compiled, respectively, on an AIX IBM work station with XL Fortran, on a Linux cluster with an Intel compiler, and on a Linux cluster with gfortran. See the section called Revision History of ZINDO-MN for detail. If you experience difficulties with compiling the program we suggest you to try the precompiled binaries.

The *zindomn-v2011.tar.gz* distribution contains a c-shell script called *veminp.csh* (find this file inside the directory *examples*). This script creates a ZINDO-MN input file *<file>.inp* to run a VEM/INDO/S2 calculation from the user-provided file *<file>* with Cartesian coordinates. If the script fails to do so, the user should create the VEM input file manually according to this manual. The syntax of *veminp.csh* is

```
./veminp.csh file DIELEC SOLN
```

Replace *file*, *DIELEC*, and *SOLN* with the name of the file, the value of *DIELEC*, and the value of *SOLN*, respectively. There is also a script (*vemrun.csh*) to iteratively run the VEM calculation. The syntax of *vemrun.csh* is

```
./vemrun.csh zindomn input output
```

Replace *zindomn* with the full-path name of the ZINDO-MN binary; replace *input* and *output* with of the names of the input and output files, respectively. Note that the directory *examples* also contains the script called *ibsfrun.csh* used by the developers, which should be ignored.

Testing

To make sure that the installation was successful, a test suite that tests many of the options available in ZINDO-MN and is supplied in the distribution. There are two test suites: one is located in the directory *testdata*, and another is located in the directory *examples*.

To run the test suite in the directory *testdata*, the user should go to this directory (by issuing the command, `cd testdata`), and run the script called *run_zindo-mn.csh* (by issuing the command, `./run_zindo-mn.csh`). This will create output files resulting from running the test suite. Each output file can be compared to reference output files supplied in the distribution of ZINDO-MN. These reference output files reside in a directory called *verify_zindo*, which is located under the *testdata* directory. This test suite includes examples of how to use the original features of ZINDO-MN (i.e., the 1999 version of ZINDO on which ZINDO-MN is based) and examples of how to use the new features (outlined in the executive summary of this manual) of ZINDO-MN. The input files that test the original features of ZINDO-MN are entitled, *DATA.Clx* (where $x = 1-26$), *DATA.Gx* (where $x = 1-15$), *DATA.Sx* (where $x = 1-23$), *DATA.PROPx* (where $x = 1$ and 2), and *DATA.RPA1*. A brief description of the specifics of these examples is included at the top of each input file.

The test suite located in the directory *examples* includes eight ZINDO-MN input files described in the section “Input and output examples.” To run this test suite the user should issue the command `./runexamples.bat` and then compare results with the output given in the section “Input and output examples.”

The string “Normal exit.” in the end of an output file indicates that the calculation was successful. Messages like “*** glibc detected *** ./zindomn: double free or corruption” can be safely ignored if the calculation was otherwise terminated normally. The c-shell script *compare.csh* located in the directory *testdata* and in the directory *examples* should be used to verify all these tests (by issuing the command, `./compare.csh`). It is

known that the following tests may fail on some platforms: *DATA.C113*, *DATA.C125*, *DATA.S20*, *DATA.X3*, *DATA.X8*.

Platforms

See the section called Revision History of ZINDO-MN.

Special notes

SCF schemes

If $JSCR = 0$, only a gas-phase calculation is done. This is the default. If $JSCR$ equals either 1 or 2, then the code does a gas-phase SCF calculation followed by a solution-phase one. Two different SCF schemes have been implemented. The standard scheme, called scheme I, uses the current solution-phase bond order matrix element values, $B_{kk'}$, at every step of the iteration. This is the scheme that was used in the calculations with which the model was parameterized. Scheme I is chosen by setting $JSCR=1$. Scheme II, on the other hand, uses the gas-phase $B_{kk'}$ values to calculate CM2 charges in solution.

Usually scheme I and scheme II give very similar results. In principle (and in practice), scheme II converges to slightly different results, and thus it could be considered to be a different model. However, in our experience the difference is usually small or even insignificant, and scheme II sometimes has better convergence properties.

The VEM model

Solvation calculations using the VEM model require a few iterations. During each iteration, an intermediate file *fort.75* will be generated for holding CM2 charges for the ground state and excited states. This file will be used as part of the input for the next iteration. Our experience shows that three iterations usually give fully converged results.

The test suite in the directory *examples* has three examples of this, *example4*, *example5*, and *example8* (see also the section “Input and output examples”). Users should also note that only the excited-state root of the CI matrix that is used to iterate the reaction field is physical. Other eigenvalues and eigenvectors are not self-consistent and are nonphysical.

Availability of QM/MM in ZINDO-MN

This version of ZINDO-MN does not support the QM/MM features in ZINDO because these calculations require files containing the desired force field potentials. Users interested in this capability should contact the developers of ZINDO.

Documentation

This manual primarily describes the Minnesota additions to ZINDO. The ZINDO-MN package also includes several useful documents regarding the use of the original components of ZINDO. These documents including a ZINDO manual are located in the *manuals* directory of the ZINDO-MN distribution package.

Revision history of ZINDO-MN

Version 1.0 (June 8, 1999)

by M. C. Zerner, J. E. Ridley, A. D. Bacon, W. D. Edwards, J. D. Head, J. McKelvey, J. C. Cuberson, P. Knappe, M. G. Cory, B. Weiner, J. D. Baker, W. A. Parkinson, D. Kannis, J. Yu, N. Roesch, M. Kotzian, T. Tamm, M. M. Karelson, X. Zheng, G. Pearl, A. Broo, K. Albert, J. M. Cullen, J. Li, G. D. Hawkins, D. A. Liotard, C. J. Cramer, and D. G. Truhlar

This version added the following capabilities to a 1999 version of ZINDO: INDO/S2, the CM2 charge model, the SM5.42R solvation model for free energies of

solvation of ground states, and the VEM42 model for the electrostatic part of the solvatochromic shift on the vertical excitation energy in liquid solution.

Version 1.0.1 (December 7, 2001)

by M. C. Zerner, J. E. Ridley, A. D. Bacon, W. D. Edwards, J. D. Head, J. McKelvey, J. C. Cuberson, P. Knappe, M. G. Cory, B. Weiner, J. D. Baker, W. A. Parkinson, D. Kannis, J. Yu, N. Roesch, M. Kotzian, T. Tamm, M. M. Karelson, X. Zheng, G. Pearl, A. Broo, K. Albert, J. M. Cullen, J. Li, G. D. Hawkins, J. D. Thompson, D. A. Liotard, C. J. Cramer, and D. G. Truhlar

This version has two bug fixes:

- A variable specific to the VEM42 model was not initialized properly during the SCF step, which led to premature exit of this step during geometry optimizations. This problem has now been fixed.
- In this version the array ETENS is dimensioned properly in subroutine HYANI. The array ETENS holds the product of the electric field gradient and the spin density matrix.

Version 1.1 (December 7, 2001)

by M. C. Zerner, J. E. Ridley, A. D. Bacon, W. D. Edwards, J. D. Head, J. McKelvey, J. C. Cuberson, P. Knappe, M. G. Cory, B. Weiner, J. D. Baker, W. A. Parkinson, D. Kannis, J. Yu, N. Roesch, M. Kotzian, T. Tamm, M. M. Karelson, X. Zheng, G. Pearl, A. Broo, K. Albert, J. M. Cullen, J. Li, G. D. Hawkins, J. D. Thompson, D. A. Liotard, C. J. Cramer, and D. G. Truhlar

This version of ZINDO-MN now assigns default values to several keywords in the \$SCRFIN input group. In particular, IAQU is set to 1 by default, and the solvent descriptors, SOLA, SOLB, SOLG, and SOLH are set to zero, by default. In addition, the documentation has been improved, and the code package and installation have been organized (see section on installation).

Version 1.2 (November 8, 2005)

by M. C. Zerner, J. E. Ridley, A. D. Bacon, W. D. Edwards, J. D. Head, J. McKelvey, J. C. Cuberson, P. Knappe, M. G. Cory, B. Weiner, J. D. Baker, W. A. Parkinson, D.

Kannis, J. Yu, N. Roesch, M. Kotzian, T. Tamm, M. M. Karelson, X. Zheng, G. Pearl, A. Broo, K. Albert, J. M. Cullen, J. Li, G. D. Hawkins, J. D. Thompson, C. P. Kelly, D. A. Liotard, C. J. Cramer, and D. G. Truhlar

This version of ZINDO-MN can be used on both IBM and non-IBM platforms. This version has been tested on the following non-IBM platforms:

- Sun Blade 2000, UltraSparc III processors, running Solaris 9, compiled with the g77 compiler version 3.2.3 (makefile.sun)
- SGI-Altix with Itanium 2 processors, running Red Hat Linux, kernel 2.4.21, compiled with the g77 compiler version 3.2.3 (makefile.ia64)
- SGI-Origin 2000, running IRIX 6.5, compiled with the gnu g77 compiler version 2.95.2 (makefile.irix)
- Netfinitiy Linux cluster running Red Hat Linux, kernel version 2.4.21, compiled with the pgf77 compiler, version 5.2.4 (makefile.linux)

Version 2010 (September 29, 2010)

by M. C. Zerner, J. E. Ridley, A. D. Bacon, W. D. Edwards, J. D. Head, J. McKelvey, J. C. Cuberson, P. Knappe, M. G. Cory, B. Weiner, J. D. Baker, W. A. Parkinson, D. Kannis, J. Yu, N. Roesch, M. Kotzian, T. Tamm, M. M. Karelson, X. Zheng, G. Pearl, A. Broo, K. Albert, J. M. Cullen, J. Li, G. D. Hawkins, J. D. Thompson, C. P. Kelly, D. A. Liotard, A. V. Marenich, C. J. Cramer, and D. G. Truhlar

The previous version was incompatible with some Linux platforms due to memory allocation problems. To resolve such problems, the following subroutines were modified (by Ben Lynch, MSI): include/bytes.cmn, io/fileop.f, util/xalloc.c. There was also an error in the VEM calculation on Linux platforms due to a bug in the subroutine ci/excsts.f/E1CSTS.

Version 2011 (April 14, 2011)

by M. C. Zerner, J. E. Ridley, A. D. Bacon, W. D. Edwards, J. D. Head, J. McKelvey, J. C. Cuberson, P. Knappe, M. G. Cory, B. Weiner, J. D. Baker, W. A. Parkinson, D. Kannis, J. Yu, N. Roesch, M. Kotzian, T. Tamm, M. M. Karelson, X. Zheng, G. Pearl, A.

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The following modifications were made:

- The code was modified according to the changes in the VEM algorithm described in the section of the manual titled “A note on the VEM model and the ZINDO-MN code.”
- We also added two c-shell scripts to create a ZINDO-MN input file from a user-provided file with Cartesian coordinates for a VEM/INDO calculation and then to run this calculation iteratively.
- The ZINDO-MN input test files DATA.MNx ($x = 1-7$) in the directory called *testdata* were substituted with the corrected and extended ZINDO-MN test suite which is now located in the directory called *examples*.
- In addition, the maximum number of SCF iterations in solution has been extended from 8 (which was not enough in many cases) to the ZINDO maximum.

The distribution contains the ZINDO-MN Fortran code recommended for compilation with either Intel+mkl or gfortran compilers and the *zindomn* binary pre-compiled using the following specifications:

- HP Linux cluster with 1,091 HP ProLiant BL280c G6 blade servers, each with two-socket, quad-core 2.8 GHz Intel "Nehalem" processors with gfortran gcc version 4.3.2 [gcc-4_3-branch revision 141291] (SUSE Linux)
- HP Linux cluster with 1,091 HP ProLiant BL280c G6 blade servers, each with two-socket, quad-core 2.8 GHz Intel "Nehalem" processors with Intel Fortran Version 11.1 and the mkl/10.2.1.017 library
- IBM RS/6000 pSeries 630 7028-6E4 AIX 5.3 with IBM(R) XL Fortran Enterprise Edition V10.1