PCET 4.0 User Manual

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About PCET

PCET (**P**roton-**C**oupled **E**lectron **T**ransfer) is a program package developed in the Sharon Hammes-Schiffer research group at the Department of Chemistry and Biochemistry, University of Notre Dame by A. Soudackov, H. Decornez and I. Rostov in the framework of the project "Theoretical Study of Proton-Coupled Electron Transfer Reactions in Solution" funded by the National Science Foundation. The package is the property of the Sharon Hammes-Schiffer research group.

Disclaimer

The developers and maintainers of the PCET 2.1 package *do not* guarantee that the package is free from errors. They *do not* accept any responsibility for any loss or damage that may result from its use. Users are not entitled to redistribute the program to third parties without consent of the owners.

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Chapter 1

Introduction

PCET is a package designed to calculate the free energy surfaces and nonadiabatic rates of proton-coupled electron transfer reactions in polar medium [1, 2, 3, 4]. The original version 2.1 combines all the original codes developed for specific model systems and written separately by different authors. The original main frame (A. Soudackov) included a simple ellipsoidal electrostatic model for solvation calculations and a four-state EVB model with standard MM parameterization for calculation of gas-phase potential. Later this code was modified (H. Decornez) to include the Voth-Schmitt EVB potential for water clusters. Another modification (I. Rostov) concerned the inclusion of Frequency Resolved Cavity Model (FRCM) for advanced solvation calculations. The combined interface to all the original codes was written by A. Soudackov and constitutes the package PCET 2.1. The latest version (3.0, A. SOudackov and E. Hatcher) includes also the additional LEPS based two-dimensional gas-phase potential, developed for enzyme applications, and effects of gating coordinate (PT donor-acceptor distance).

1.1 Functionality

1.1.1 General features

- Gas-phase potentials

  - four state EVB potential with standard MM parameterization of EVB matrix elements [2]
  - Voth-Schmitt multistate EVB potential for water clusters [5]
  - LEPS based four-state EVB potential for five-site linear model (enzyme applications).

- Solvent models

    - continuum electrostatic model with ellipsoidal cavity [6]
    - advanced continuum Frequency Resolved Cavity Model (FRCM) with cavities of molecular shape [7]

- Free energy surfaces as functions of scalar solvent coordinates (on the grid or along a given path)

    - diabatic and adiabatic free energy curves for single ET reaction between any two EVB states
    - adiabatic electronic/proton vibrational free energy surfaces (FES)
    - ET diabatic electronic/proton vibrational FESs
    - diabatic electronic/proton vibrational FESs

- Rates

    - nonadiabatic rates for single ET and PT reactions between any two EVB states
    - nonadiabatic rates as non-radiative transitions between two sets of ET diabatic two-dimensional free energy surfaces [3]
        * averaged over gating (donor-acceptor) distances
        * with quantum description of the gating mode

- solvent mediated nonadiabatic couplings between adiabatic electronic/proton

$$/gating$$

vibrational states

1.1.2 Quantization algorithm

The one-dimensional Schrödinger equations for the proton and gating motion are solved numerically using the Discrete Fourier Grid Hamiltonian representation [8]

1.1.3 Limitations

There are two main limitations in the current version of PCET program:

- the four-state MS-EVB model is implemented. It means that maximum two coupled charge transfer processes can be described. Accordingly, maximum four different charge distributions in the reacting system can be defined.

- only one quantum particle moving in one dimension and one gating coordinate (proton donor-acceptor distance) can be taken into account explicitly.

1.2 Programming Language

All the routines in the current version of PCET are written mostly in FORTRAN-77. Memory allocation is done using FORTRAN-90 rules and syntaxis. FORTRAN-90 features used in FRCM related routines were removed to maintain the overall consistence.

1.3 Target Computers

Currently, PCET 3.0 can be compiled for the following platforms:

- SGI under IRIX 6.4/6.5 (SGI f90 compiler)

- LINUX 2.2.14 (Portland Group compiler pgf90)

1.4 Required External Libraries

No libraries required.

1.5 Arithmetic Precision

All real variables and parameters are specified as real*8 (64-bit).

1.6 Units

The program uses kcal/mol for energy and Angströms for length. All the charges and masses are in atomic units.

1.7   The PCET 2.1 directory structure

subdirectory	contents
bin	executable (`pcet2.1.xxx`)
include	include files (`*.h, *.inc`)
source	FORTRAN source files, `Makefile`
docs	documentation (this file)
work	input and output files for testing

Chapter 2

Theoretical Background

2.1 Four-state Continuum Model for PCET reactions

The electronic Hamiltonian of the PCET system (solute with the surrounding continuum medium) is represented in the basis of the following four valence bond (VB) states:

$$
\begin{array}{llllllll}
(1a) & D_e{}^{\ominus} & - & {}^{\oplus}D_p & H & \cdots & \cdots & A_p{}^{\ominus} & - & A_e \\
(1b) & D_e{}^{\ominus} & - & D_p & \cdots & \cdots & H & A_p & - & A_e \\
(2a) & D_e & - & {}^{\oplus}D_p & H & \cdots & \cdots & A_p{}^{\ominus} & - & A_e{}^{\ominus} \\
(2b) & D_e & - & D_p & \cdots & \cdots & H & A_p & - & A_e{}^{\ominus}.
\end{array}
\tag{2.1}
$$

Here the symbols D_e and A_e represent a general electron donor and acceptor, D_p and A_p represent a general proton donor and acceptor, and H represents the transferring proton. The VB states are labeled as follows: a denotes that the proton is bonded to its donor while b denotes that the proton is bonded to its acceptor, and 1 denotes that the electron is localized on its donor while 2 denotes that the electron is localized on its acceptor. Thus, a and b indicate the proton transfer (PT) state, and 1 and 2 indicate the electron transfer (ET) state.

The electrostatic interaction of the solute with the continuum solvent is described in terms of the two scalar solvent variables z_p and z_e corresponding

to the PT and ET processes, respectively:

$$z_p = \int d\mathbf{r} \, [\rho_{1b}(\mathbf{r}) - \rho_{1a}(\mathbf{r})]\phi_{\text{in}}(\mathbf{r})$$

$$z_e = \int d\mathbf{r} \, [\rho_{2a}(\mathbf{r}) - \rho_{1a}(\mathbf{r})]\phi_{\text{in}}(\mathbf{r}), \tag{2.2}$$

where $\rho_{ii}(\mathbf{r})$ is the total charge density of VB state i and $\phi_{\text{in}}(\mathbf{r})$ is the inertial polarization field of the solvent.

The electronic Hamiltonian matrix representing the free energy of the PCET system as a function of two solute nuclear coordinates (including the coordinate r_p of the quantum particle and the gating coordinate R defined as the proton donor-acceptor distance) and two solvent variables z_p and z_e has a form:

$$\mathbf{H}(r_p, R, z_p, z_e) = \mathcal{S}(r_p, R, z_p, z_e)\mathbf{I} + \mathbf{H}_o(r_p, R) + \begin{pmatrix} 0 & 0 & 0 & 0 \\ 0 & z_p & 0 & 0 \\ 0 & 0 & z_e & 0 \\ 0 & 0 & 0 & z_p + z_e \end{pmatrix}. \tag{2.3}$$

The transformed self-energy $\mathcal{S}(r_p, R, z_p, z_e)$ of the solvent inertial polarization field is expressed as

$$\mathcal{S}(r_p, R, z_p, z_e) = \frac{1}{2} \sum_{i,j=1b,2a} \left\{ \left[y'_i + t'_{1a,i}(r_p, R)\right] \left[\mathbf{t}'_t(r_p, R)^{-1}\right]_{i,j} \left[y'_j + t'_{1a,j}(r_p, R)\right] \right\} - \frac{1}{2} t'_{1a,1a}(r_p, R), \tag{2.4}$$

where the summation runs over valence bond states $1b$ and $2a$, the truncated reorganization energy matrix $\mathbf{t}'_t$ has dimensions 2×2 corresponding to these two states, and $(z_p, z_e) \equiv (y'_{1b}, y'_{2a})$. The inertial reorganization energy matrix elements t'_{ij} can be expressed as

$$t'_{ij} = -\int d\mathbf{r} \, \nu_{jj}(\mathbf{r})[\hat{K}(\epsilon_o) - \hat{K}(\epsilon_\infty)]\nu_{ii}(\mathbf{r}), \tag{2.5}$$

where $\hat{K}(\epsilon)$ is the dielectric Green function for the medium with dielectric constant ϵ and

$$\nu_{1a,1a}(\mathbf{r}) = \rho_{1a,1a}(\mathbf{r})$$

$$\nu_{ii}(\mathbf{r}) = \rho_{ii}(\mathbf{r}) - \rho_{1a,1a}(\mathbf{r}) \quad (i = 1b, 2a, 2b). \tag{2.6}$$

Finally, $\mathbf{H}_o(r_p, R)$ is the gas phase electronic Hamiltonian matrix.

The free energy surfaces of the system in space of the solute nuclear coordinates and two solvent coordinates are obtained by the diagonalization of the matrix (2.3).

2.2   Mixed Electronic/Vibrational Free Energy Surfaces

To take into account the quantum nature of the transferring proton (or other light particle) with the coordinate r_p one needs to solve the Schrödinger equation

$$H^{\text{total}}(\mathbf{r}^{(e)}, r_p, R, z_p, z_e)\Phi_n(\mathbf{r}^{(e)}, r_p; R, z_p, z_e) = E_n(R, z_p, z_e)\Phi_n(\mathbf{r}^{(e)}, r_p; R, z_p, z_e)$$
$$(2.7)$$

Here H^{total} is the total Hamiltonian for fixed solvent and gating coordinates (R, z_p, z_e) and can be expressed as

$$H'(\mathbf{r}^{(e)}, r_p, R, z_p, z_e) = -\frac{\hbar^2}{2m_p}\frac{\partial^2}{\partial r_p^2} + \mathbf{H}(\mathbf{r}^{(e)}, r_p, R, z_p, z_e) \qquad (2.8)$$

where the first term is the kinetic energy of the transferring proton and the second term is the electronic Hamiltonian defined in Eq. 2.3. The quantities $E_n(R, z_p, z_e)$ represent the free energies of the mixed *electronic/vibrational* (vibronic) states $\Phi_n(\mathbf{r}^{(e)}, r_p; R, z_p, z_e)$.

In the case of the quantization along the gating coordinate...

2.2.1   Methods of Solution of Eq.(2.7)

In the program PCET, three different methods of solution of the equation (2.7) are implemented. In all these methods the total Hamiltonian is represented in the basis of the products of electronic and vibrational wavefunctions.

Method 1: based on diabatic electronic states

In this approach the mixed electronic/proton vibrational adiabatic states are expanded in a basis of products of diabatic electronic states and corresponding adiabatic proton vibrational states. The approach consists of three steps.

The first step is to calculate the energies of the electronic diabatic states for fixed solvent coordinates (z_p, z_e) for all points r_p along a one-dimensional grid between the proton donor and acceptor. The energy of the diabatic electronic state i is

$$E_i^{(\text{dia})}(r_p, z_p, z_e) = H_{ii}(r_p, z_p, z_e) \qquad (2.9)$$

The second step is to calculate the proton vibrational adiabatic states $\phi_\mu^{(i)}(r_p; z_p, z_e)$ for fixed solvent coordinates for each diabatic electronic state i by numerically solving the one-dimensional Schrödinger equation

$$\left(-\frac{\hbar^2}{2m_p}\frac{\partial^2}{\partial r_p^2} + E_i^{(\text{dia})}\right)\phi_\mu^{(i)}(r_p; z_p, z_e) = \epsilon_\mu^{(i)}(z_p, z_e)\phi_\mu^{(i)}(r_p; z_p, z_e). \quad (2.10)$$

This equation is solved by expanding the proton vibrational states on a grid along the axis between the proton donor and acceptor and implementing standard discrete Fourier grid techniques.

The third step in this approach is to calculate the numerically exact mixed electronic/proton vibrational adiabatic states by expanding them in terms of basis states each comprised of a product of an electronic diabatic state i and a proton vibrational adiabatic state $\phi_\mu^{(i)}$. The mixed electronic/vibrational states are calculated by solving the matrix equation

$$\mathbf{H}^{\text{total}}\mathbf{D} = \mathbf{D}\mathbf{E}, \quad (2.11)$$

where $\mathbf{D}$ has elements $D_{i\mu,n}$, $\mathbf{E}$ is diagonal with elements E_n, and the matrix elements of the Hamiltonian $\mathbf{H}^{\text{total}}$ are

$$H_{i\mu,j\nu}^{\text{total}} = \delta_{ij}\delta_{\mu\nu}\epsilon_\mu^{(i)}(z_p, z_e) + (1 - \delta_{ij})\left\langle \phi_\mu^{(i)} \left| H_{ij} \right| \phi_\nu^{(j)} \right\rangle_p. \quad (2.12)$$

(Here $\langle \ldots \rangle_p$ indicates integration over r_p.) The energies of the mixed electronic/proton vibrational adiabatic states can be calculated as functions of the two solvent scalar variables z_p and z_e by following these three steps for solvent coordinates (z_p, z_e) on a two-dimensional grid.

Method 2: based on adiabatic electronic states

In this approach the mixed electronic/proton vibrational adiabatic states are expanded in a basis of double adiabatic states. The approach consists of three steps. The first step is to calculate the electronic adiabatic states $\Psi_k(\mathbf{r}^{(e)}; r_p, z_p, z_e)$ for fixed solvent coordinates (z_p, z_e) for all points r_p along a one-dimensional grid between the proton donor and acceptor. The electronic wavefunction Ψ_k is a linear combination of the four valence bond states (1a, 1b, 2a, 2b). The energy of electronic state k is $\mathcal{U}_k(r_p, z_p, z_e)$ obtained by diagonalizing the matrix $\mathbf{H}$ defined in Eq. 2.3.

The second step of this prescription is to calculate the proton vibrational adiabatic states $\phi_\mu^{(k)}(r_p; z_p, z_e)$ for fixed (z_p, z_e) for each relevant adiabatic

electronic state k by numerically solving the one-dimensional Schrödinger equation

$$H_p^{(k)}\phi_\mu^{(k)}(r_p; z_p, z_e) = \epsilon_\mu^{(k)}(z_p, z_e)\phi_\mu^{(k)}(r_p; z_p, z_e), \qquad (2.13)$$

where the proton Hamiltonian for the electronic state k is defined as

$$H_p^{(k)} = -\frac{\hbar^2}{2m_p}\frac{\partial^2}{\partial r_p^2} + \mathcal{U}_k(r_p, z_p, z_e). \qquad (2.14)$$

The third step of the prescription is to calculate the mixed electronic/proton vibrational adiabatic states Φ_n by expanding them in a basis of double adiabatic states $\xi_{k\mu}$:

$$\Phi_n(\mathbf{r}^{(e)}, r_p; z_p, z_e) = \sum_{k\mu} D_{k\mu,n}\xi_{k\mu}(\mathbf{r}^{(e)}, r_p; z_p, z_e) \qquad (2.15)$$

where

$$\xi_{k\mu}(\mathbf{r}^{(e)}, r_p; z_p, z_e) = \Psi_k(\mathbf{r}^{(e)}; r_p, z_p, z_e)\phi_\mu^{(k)}(r_p; z_p, z_e). \qquad (2.16)$$

The mixed electronic/vibrational states are calculated by solving the matrix equation

$$\mathbf{H}^{\text{total}}\mathbf{D} = \mathbf{D}\mathbf{E}, \qquad (2.17)$$

where $\mathbf{D}$ has elements $D_{k\mu,n}$, $\mathbf{E}$ is diagonal with elements E_n, and the matrix elements of the Hamiltonian $\mathbf{H}^{\text{total}}$ are

$$H_{k\mu,l\nu}^{\text{total}} = \langle\xi_{k\mu}|H^{\text{total}}|\xi_{l\nu}\rangle. \qquad (2.18)$$

It is straightforward to show that

$$H_{k\mu,l\nu}^{\text{total}} = \delta_{kl}\delta_{\mu\nu}\epsilon_\mu^{(k)}(z_p, z_e) - \frac{\hbar^2}{m_p}\left\langle\phi_\mu^{(k)}\left|d_{kl}^{(ep)}\frac{\partial\phi_\nu^{(l)}}{\partial r_p}\right.\right\rangle_p - \frac{\hbar^2}{2m_p}\langle\phi_\mu^{(k)}|g_{kl}^{(ep)}\phi_\nu^{(l)}\rangle_p,$$

$$(2.19)$$

where

$$d_{kl}^{(ep)}(r_p, z_p, z_e) = \left\langle\Psi_k\left|\frac{\partial\Psi_l}{\partial r_p}\right.\right\rangle_e \qquad (2.20)$$

and

$$g_{kl}^{(ep)} = \left\langle\Psi_k\left|\frac{\partial^2\Psi_l}{\partial r_p^2}\right.\right\rangle_e. \qquad (2.21)$$

In these equations $\langle\rangle_{ep}$, $\langle\rangle_e$, and $\langle\rangle_p$ indicate integration over $(\mathbf{r}^{(e)}, r_p)$, $\mathbf{r}^{(e)}$, and r_p, respectively.

The energies of the mixed electronic/proton vibrational adiabatic states are calculated as functions of the two solvent scalar variables z_p and z_e by following the above three steps for solvent coordinates (z_p, z_e) on a two-dimensional grid.

Method 3: double-adiabatic approach

This method is actually an approximation to the method 2 described above. It is assumed that the nonadiabatic coupling terms d_{kl} and g_{kl} defined in Eqs.(2.20) and (2.21) are negligibly small and the total Hamiltonian matrix is diagonal in the double adiabatic representation. Thus the free energies are equal to the double-adiabatic energies $\epsilon_\mu^{(k)}(z_p, z_e)$.

2.2.2   Free Energy Surfaces in Different Representations

In some specific cases it is useful to analyze different types of free energy electronic/vibrational surfaces. The program PCET can calculate free energies in three different representations.

Adiabatic Free Energy Surfaces (`ADIAB`)

This is a most general representation. The corresponding states are *adiabatic* with respect to the solvent motions and all the couplings between the electronic EVB states as well as all the nonadiabatic couplings between electronic and proton motions are taken into account explicitly. The free energies are calculated as eigenvalues of the total Hamiltonian H^{total}.

ET-Diabatic Free Energy Surfaces (`DIAB2`)

This representation is natural for the systems with strongly nonadiabatic ET and adiabatic PT when the couplings between (1a/1b) and (2a/2b) electronic VB states are small compared to the thermal energy $k_{\text{B}}T$. The two sets of the corresponding free energies and mixed electronic/vibrational ET diabatic states are obtained by applying one of the above mentioned methods to (1a/1b) or (2a/2b) blocks of the electronic Hamiltonian matrix (2.3).

Diabatic Free Energy Surfaces (`DIAB4`)

This representation is natural for the systems with strongly nonadiabatic ET and PT when all the couplings between electronic VB states are small compared to the thermal energy $k_{\text{B}}T$. Formally, it corresponds to the electronic Hamiltonian matrix (2.3) with zero off-diagonal matrix elements.

2.3   Gas Phase Model Potentials

The model gas phase potentials implemented in the program are based on the four-state EVB model with electronic basis states defined in Eq.(2.1). They differ by the parameterization of the EVB matrix elements.

2.3.1   Standard MM parameterization (MM1)

The matrix elements of the gas phase Hamiltonian are approximated by standard molecular mechanical terms fit to electronic structure calculations for the gas phase solute. The diagonal matrix elements are expressed as

$$
\begin{aligned}
(h_0)_{1a1a}(r_p) &= U_{NH}^{\text{Morse}}(r_p) + U_{OH}^{\text{rep}}(r_p) + U_{1a}^{\text{Coul}}(r_p) \\
(h_0)_{1b1b}(r_p) &= U_{OH}^{\text{Morse}}(r_p) + U_{NH}^{\text{rep}}(r_p) + U_{1b}^{\text{Coul}}(r_p) + \Delta_{1b} \\
(h_0)_{2a2a}(r_p) &= U_{NH}^{\text{Morse}}(r_p) + U_{OH}^{\text{rep}}(r_p) + U_{2a}^{\text{Coul}}(r_p) + \Delta_{2a} \\
(h_0)_{2b2b}(r_p) &= U_{OH}^{\text{Morse}}(r_p) + U_{NH}^{\text{rep}}(r_p) + U_{2b}^{\text{Coul}}(r_p) + \Delta_{2b}
\end{aligned}
\tag{2.22}
$$

where
$$
U_{AH}^{\text{Morse}}(r_p) = D_{AH}\left(1 - e^{-\beta_{AH}(R_{AH} - R_{AH}^o)}\right)^2
\tag{2.23}
$$

is a Morse potential for an A-H bond,

$$
U_{AH}^{\text{rep}}(r_p) = D'_{AH} e^{-\beta'_{AH} R_{AH}}
\tag{2.24}
$$

is a repulsion term between non-bonded atoms A and H, and

$$
U_i^{\text{Coul}}(r_p) = \frac{1}{2}\sum_{k \neq l} \frac{q_k^i q_l^i}{R_{kl}}
\tag{2.25}
$$

is a Coulomb interaction potential between the point charges (where the summation is over sites k, l and q_k^i is the charge on site k for VB state i). In all of these expressions R_{kl} is the distance between sites k and l. The couplings between the VB states are expressed as

$$
\begin{aligned}
(h_o)_{1a,1b}(r_p) &= V^{PT1}\exp^{-\gamma_{\text{PT}}(r_p - r_p^{\text{PT}})^2} \\
(h_o)_{2a,2b}(r_p) &= V^{PT2}\exp^{-\gamma_{\text{PT}}(r_p - r_p^{\text{PT}})^2} \\
(h_o)_{1a,2a}(r_p) &= (h_o)_{1b,2b}(r_p) = V^{ET}\exp^{-\gamma_{\text{ET}}(r_p - r_p^{\text{ET}})^2} \\
(h_o)_{1a,2b}(r_p) &= (h_o)_{1b,2a}(r_p) = V^{EPT}\exp^{-\gamma_{\text{EPT}}(r_p - r_p^{\text{EPT}})^2} .
\end{aligned}
\tag{2.26}
$$

2.3.2 Two-dimensional LEPS potential

2.3.3 Voth-Schmitt parameterization for water clusters

2.4 Solvation models

2.4.1 Ellipsoidal Model

In this model the solute is represented by a set of point charges located on one axis. Different charge distributions corresponding to VB basis states are modelled by different magnitudes of point charges. The point charges representing the solute are placed on the main axis of an axially symmetrical ellipsoidal cavity embedded in a dielectric continuum solvent characterized by the inertial (ϵ_0) and electronic (optical) (ϵ_∞) dielectric constants (see Fig. 2.1).

The total polarization potential $\phi(\mu, \lambda)$ at the point (μ, λ) (elliptical co-

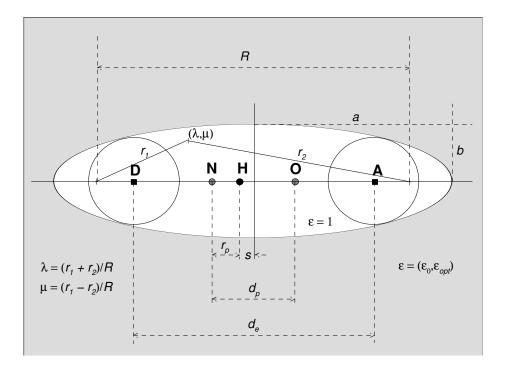Figure 2.1: Ellipsoidal model cavity and its geometrical parameters.

ordinates) inside the cavity can be expressed as[6]

$$\phi(\mu, \lambda) = \sum_{n=0}^{\infty} B_n(\epsilon_0) P_n(\mu) P_n(\lambda) \tag{2.27}$$

where B_n are constants and P_n are the Legendre functions of the first kind. The expression for the coefficients B_n is readily obtained from traditional electrostatics:

$$B_n = \frac{2(2n+1)\beta_n}{R} \left(\frac{1}{\epsilon_0} - 1 \right) \frac{Q_n(\lambda_0)}{P_n(\lambda_0)} \left[1 - \frac{1}{\epsilon_0} \frac{\lambda_0 - P_{n-1}(\lambda_0)/P_n(\lambda_0)}{\lambda_0 - Q_{n-1}(\lambda_0)/Q_n(\lambda_0)} \right]^{-1} \tag{2.28}$$

Here R is the interfocal distance, λ_0 defines the ellipsoid boundary, Q_n are the Legendre functions of the second kind, and β_n is given by the sum over the N point charges with magnitudes q_k and positions on the axis μ_k

$$\beta_n = \sum_{k=1}^{N} q_k P_n(\mu_k) \tag{2.29}$$

The inertial polarization field is calculated as a difference between the total field and the electronic polarization field:

$$\phi_{\text{in}} = \phi - \phi_{\infty} \tag{2.30}$$

where ϕ_{∞} is obtained using Eqs.(2.27-2.28) by substituting ϵ_0 in Eq.(2.28) with ϵ_{∞}.

The reorganization energy matrix elements are calculated then on the grid along the proton coordinate by using standard definitions[1]:

$$t_{ij} = -\sum_k q_k^{(i)} (\phi^{(j)} - \phi_{\infty}^{(j)}) \tag{2.31}$$

$$t_{ij}^{(\infty)} = -\sum_k q_k^{(i)} \phi_{\infty}^{(j)} \tag{2.32}$$

where indices i and j label charge distributions corresponding to the VB basis states.

2.4.2 FRCM

Relevant references:

- Chudinov, Napolov, and Basilevsky, Chemical Physics **160**, 41-54 (1992).

- Basilevsky, Rostov, and Newton, Chemical Physics **232**, 189-199 (1998).

- Soudackov and Hammes-Schiffer, J. Chem. Phys. **111**, 4672 (1999).

Description of algorithm

Reorganization energy matrix elements

The multistate continuum theory requires the calculation of the solvent reorganization energy matrix elements defined as

$$t_{ij} = -\int d\mathbf{r}\, \rho_i \hat{\mathcal{K}}_{\mathrm{in}} \rho_j = -\int d\mathbf{r}\, \rho_i \phi_j^{(\mathrm{in})}, \ \ \phi_j^{(\mathrm{in})} = \hat{\mathcal{K}}_{\mathrm{in}} \rho_j \tag{2.33}$$

and

$$t_{ij}^{(\infty)} = -\int d\mathbf{r}\, \rho_i \hat{\mathcal{K}}_{\infty} \rho_j = -\int d\mathbf{r}\, \rho_i \phi_j^{(\infty)}, \ \ \phi_j^{(\infty)} = \hat{\mathcal{K}}_{\infty} \rho_j. \tag{2.34}$$

Here the operator $\hat{\mathcal{K}}_{\infty} = \hat{\mathcal{K}}(\epsilon_{\infty})$ and $\hat{\mathcal{K}}_{\mathrm{in}} = \hat{\mathcal{K}}(\epsilon_o) - \hat{\mathcal{K}}(\epsilon_{\infty})$, where $\hat{\mathcal{K}}(\epsilon)$ is a dielectric Green function for the medium with dielectric constant ϵ and ϵ_o and ϵ_{∞} are the static and electronic dielectric constants, respectively. The calculation of these reorganization energies requires the calculation of the potentials $\phi_j^{(\infty)} = \hat{\mathcal{K}}(\epsilon_{\infty}) \rho_j$ and $\phi_j^{(\mathrm{tot})} = \hat{\mathcal{K}}(\epsilon_o) \rho_j$ caused by the charge density ρ_j in a dielectric continuum with dielectric constant ϵ_{∞} and ϵ_o, respectively. The inertial potential may be calculated from these two potentials:

$$\phi_j^{(\mathrm{in})} = \phi_j^{(\mathrm{tot})} - \phi_j^{(\infty)}. \tag{2.35}$$

The FRCM method is used to calculate these potentials.

Calculation of the electrostatic potential due to solvent response

The standard PCM method is used to calculate the electronic solvent potential $\phi_j^{(\infty)}$. In this method, the entire charge density ρ_j is placed in a cavity of arbitrary shape with surface S. The dielectric constant is equal to unity inside the cavity and is equal to ϵ_{∞} outside the cavity. The electronic solvent potential $\phi_j^{(\infty)}$ is calculated by solving the Poisson equation with the appropriate boundary conditions at the surface of the cavity. (Note that the total potential used in the Poisson equation is the sum of the potential due to the charge density ρ_j in a vacuum and the solvent potential $\phi_j^{(\infty)}$ describing the potential due to the solvent response to the density ρ_j.) The solvent potential may be expressed in terms of a surface charge density σ_j on the surface S. Thus, the problem is reduced to the calculation of this surface charge density σ_j corresponding to the charge density ρ_j. The surface charge

density σ_j may be defined in terms of a standard integral equation, which must be solved iteratively.

The FRCM method is used to calculate the total solvent potential $\phi_i^{(\text{tot})}$. In this method, two cavities are formed around the charge density ρ_j. This leads to an inner surface S_1 and an outer surface S_2. The entire charge density is assumed to be contained inside the inner cavity. The dielectric constant is equal to unity inside the inner cavity, to ϵ_∞ in the region between the two surfaces S_1 and S_2, and to ϵ_o in the region outside the outer cavity. The solvent potential $\phi_j^{(\text{tot})}$ is calculated by solving the Poisson equation with the appropriate boundary conditions at the two surfaces S_1 and S_2. (Again, note that the total potential used in the Poisson equation is the sum of the potential due to the charge density ρ_j in a vacuum and the solvent potential $\phi_j^{(\text{tot})}$ describing the potential due to the solvent response to the density ρ_j.) The solvent potential may be expressed in terms of two surface charge distributions $\sigma_j^{(1)}$ and $\sigma_j^{(2)}$ on the surfaces S_1 and S_2, respectively. In this case, the problem requires the calculation of both surface charge distributions corresponding to the charge density ρ_j. These surface charge densities may be defined in terms of integral equations which must be solved iteratively.

In order to numerically solve the integral equations for both PCM and FRCM, the surface integrals are computed by dividing the surface into small pieces. These surface elements are denoted "tesserae" or "sectors" (where the terms are used interchangably, although a sector actually refers to a three-dimensional segmenet and a tesserae actually refers to only the surface element). The convergence of the iterative solution of the Poisson equation is determined by the dimensionless parameter SELFCR, where the convergence criterion is defined to be SELFCR$\times 10^{-4}$ for the outer cavity and SELFCR$\times 10^{-5}$ for the inner cavity. The default is SELFCR=2.0. In past versions, the keyword PRECISE decreases this to SELFCR=0.2, but this word should not be used in the current version. After the surface charge density has converged, it is renormalized according to the total charge of the solute. If the total surface charge computed from the numerical surface charge density differs from the value determined by the total solute charge by more than CHDIFF directly prior to the renormalization of the surface charge density, an error message is printed. The default value is CHDIFF=0.1. The maximum number of iterations is ITSE, after which an error message is printed and the program is stopped. The default value is ITSE=15.

Thus, the calculation of the electronic and inertial potentials requires

the following steps:

1. Generate the surfaces of the two cavities.

2. Generate the tesserae independently for the two cavities.

3. Numerically solve the Poisson equation using PCM for the inner cavity surrounded by solvent with dielectric constant ϵ_∞ to obtain the electronic potential $\phi_j^{(\infty)}$.

4. Numerically solve the Poisson equation using FRCM for the two cavities with solvent of dielectric constant ϵ_∞ in between the two surfaces and ϵ_o outside both cavities to obtain the total potential $\phi_j^{(\text{tot})}$.

5. Calculate the inertial potential $\phi_j^{(\text{in})} = \phi_j^{(\text{tot})} - \phi_j^{(\infty)}$.

6. Use these potentials to calculate the electronic and inertial reorganization energy matrix elements.

Generation of surfaces

In FRCM, the inner cavity is generated by placing a sphere centered on each atom with radius κr_{vdw}, where r_{vdw} is the van der Waals radius for the specific atom and κ is independent of the solvent with a default value of 0.9. In the FRCM program, the surface of the inner cavity may be smoothed by including additional spheres. The key words SMOOTH and NOSMOOTH denote cavity smoothing or the absence of cavity smoothing. The default is to include smoothing. The parameter SOLRD defines the effective radius (in Angstroms) of the solvent molecules and is used to calculate the excluded volume at the seam of a pair of overlapping spheres. The default value is SOLRD=1 Å. The parameter EXVOL defines the minimum excluded volume (in cubic Angstroms) at such a seam for which an auxiliary sphere is added during smoothing. The default value is EXVOL=1 Å^3. If EXVOL (or SOLRD) is large enough, the effect is the same as using the key word NOSMOOTH. The outer sphere cavity is generated by adding δ to the radius of each sphere used to create the inner cavity (including the spheres added for smoothing). In general, δ depends on the solvent.

Generation of tesserae/sectors

The premise of the method for generation of the tesserae (or sectors) is that the surface charges change more rapidly closer to the seam of the intersection

between two spheres. Thus, the surface elements should be chosen to be smaller in the regions of close contact of the spheres. The following three steps are used to generate the tesserae.

1. The first step is to create a network of A-sectors for each pair of spheres. These sectors are smaller in contact regions (i.e., where the spheres overlap) and larger in regions near the poles. The tesserae are created through a series of rings moving from a contact region to a pole. The tesserae (or sectors) are defined in terms of the standard polar angles θ and ϕ, where $0 < \theta < 180^o$ and $0 < \phi < 360^o$, and θ is measured relative to the axis connecting the centers of the pair of spheres. The parameters that determine the sizes of the A-sectors and the basic procedure used to create the A-sectors are as follows.

   - The parameters that determine the sizes of the A-sectors are MODFE1 and MODFE2 for the inner and outer surfaces, respectively. This discussion will use MODFE1 as the example. The maximum angular step size $\Delta\theta$ for θ is defined as

$$N = 400/3/\text{MODFE1}. \qquad (2.36)$$

   For the default value of MODFE1=6, $N = 22.2^o$. The first two rings near the contact region have $\Delta\theta = 0.6N$ and $\Delta\theta = 0.9N$, respectively, and the remaining rings have $\Delta\theta = N$. The values for these angular step sizes are stored in the array DDTET, where the first element is $0.6N$, the second element is $0.9N$, and the remaining elements are N. The number of elements is such that the sum of all angles is less than 180°. Thus, for MODFE1=6, DDTET=(13.3, 20.0, 22.2, 22.2, 22.2, 22.2, 22.2, 22.2). The angle ϕ has the same angular step size $\Delta\phi$ as θ except for the first two rings, where $\Delta\phi = 1.33\Delta\theta$ and $\Delta\phi = 1.28\Delta\theta$, respectively.

   - The A-sectors are created for each pair in the following manner. First, the angle in θ for the overlap between the spheres is determined to exclude it from consideration. Second, the sectors are created through a series of rings, using the angular step sizes from the array DDTET, starting at the contact region and moving toward the pole. The sectors are renormalized to render the total sum of angular steps for θ and ϕ 180° and 360°, respectively. Since this procedure is done for each pair of spheres, for each sphere there is a combination of overlapping networks of A-sectors due to all of its neighbors.

- The relation between MODFE1 and MODFE2 is critical to the numerical accuracy. Typically, for MODFE1=MODFE2, the number of tesserae is significantly greater for the inner surface than for the outer surface. This results from the greater overlap between the larger spheres for the outer surface, leading to a larger value of the excluded angle θ and thus to a smaller number of tesserae for each pair of spheres. In addition, the spheres added for smoothing of the inner surface do not contribute as much to the surface area of the outer cavity. Furthermore, for MODFE1=MODFE2, the tesserae are larger in surface area for the outer surface than for the inner surface. This inconsistency between the size and number of tesserae on the two surfaces leads to numerical instabilities. One approach is to choose MODFE2 such that the maximum area of the tesserae for the inner and outer surfaces is approximately equal. This can be achieved using the equation

$$\text{MODFE2} = \text{MODFE1} * (\kappa r_{vdw} + \delta)/(\kappa r_{vdw}) \qquad (2.37)$$

for a typical value of r_{vdw} for the system of interest. Another approach is to choose MODFE2 such that the number of tesserae on the inner and outer surfaces is nearly equal.

2. The second step to create a network of small elements, called B-sectors. These are also defined in terms of the angles θ and ϕ. The angular step sizes are defined in terms of NTETFI1 and NTETFI2 for the inner and outer cavities, respectively. This discussion will use NTETFI1 as the example. The angular step sizes are defined as

$$\begin{aligned} \Delta\phi &= 360/(\text{NTETFI1} * 120) & (2.38) \\ \Delta\theta &= 180/(\text{NTETFI1} * 60). & (2.39) \end{aligned}$$

The default is NTETFI1=NTETFI2=1, which leads to step sizes of 3°. This leads to 7200 B-sectors per sphere.

3. In the third step of the generation of the tesserae, the A-sectors and the B-sectors are used to construct a unique set of sectors completely covering the whole surface, called the C-sectors. In this procedure, each B-sector is related to the A-sector derived from the neighboring sphere closest to it. Thus, each B-sector is uniquely related to an A-sector. The B-sectors related to the same A-sector are combined as a cluster called a C-sector. The network of C-sectors completely and

uniquely covers the cavity surface. In order to decrease the total number of C-sectors, some of the C-sectors are combined with neighboring smaller ones.

2.5   Discrete Fourier Grid Algorithm

2.6   Nonadiabatic Rate Calculation

The program PCET 2.0 calculates the nonadiabatic rate of the PCET reaction using the expression derived in Ref. [3] for the case of nonadiabatic ET and adiabatic PT. Note that only in this regime the results are meaningful. The rate expression reads

$$k = \frac{2\pi}{\hbar} \sum_{\mu} P_{\mu}^{I} \sum_{\nu} V_{\mu\nu}^2 (4\pi \lambda_{\mu\nu} k_{\mathrm{B}} T)^{-1/2} \exp\left\{ -\frac{(\Delta G_{\mu\nu}^0 + \lambda_{\mu\nu})^2}{4\lambda_{\mu\nu} k_{\mathrm{B}} T} \right\}. \quad (2.40)$$

Here the indices μ and ν run over the reactant and product mixed electronic/vibrational states, respectively. These states are calculated in the `DIAB2` representation and correspond to the reactant and product states in the ET reaction. The couplings $V_{\mu\nu}$ are calculated at the intersection points along the straight line connecting the minima of reactant and product two-dimensional surfaces. The two-dimensional reorganization energies are calculated either numerically (from actual two-dimensional surface according to Marcus definition) or analytically using the expression (55) from Ref. [3]. The activation energies in the exponential of Eq.(2.40) also can be calculated either numerically (from the intersecting surfaces) or analytically using the Marcus-like relation.

Chapter 3

Compiling and Execution

3.1 Compiling PCET 2.0

To compile PCET 2.0 program for a specific platform you need change to
the `source` directory, then copy `Makefile.xxx` to `Makefile`, for example

```
cp Makefile.xxx Makefile

make all
```

where `<xxx>` must be substituted by the platform-specific suffix. With the
present version two makefiles are supplied:

`Makefile.sgi` - for SGI platforms

`Makefile.lnx` - for LINUX platforms with Portland Group
FORTRAN compiler `pgf77`

    This will initiate compiling and linking of the program. First, the make-
file will build an object library containing all the object files except the
object file for the main program. Then the makefile will combine the main
object file with the library and produce the executable `pcet2.0.xxx` which
will be placed in the `bin` directory.

    When you modify the include files with parameters and array dimensions,
you **must** recompile all the source codes and build a new library. To remove
the old object library run the command

```
make clean
```

3.2   Running PCET 2.0

You can run PCET 2.0 program from any directory you wish provided that the path to the executable is listed in your `PATH` variable or you have a link to the executable in your current directory.

You will need four mandatory (and maybe more optional) input files in your current directory. The main input file (control file) with arbitrary name contains the control information (keywords) about the jobs you want to run. It contains also the names of other optional input files you may want to use. The other three mandatory files are the files with geometry specifications for gas phase and solvation calculations (you can use the same file for both gas phase and solvation calculations) and the file with parameters of the gas phase potential. The names of these files are specified in the keyword section of the control input file. The detailed information about the structure of the input files is given in the next chapter.

To initiate execution you have to run the command

```
pcet2.0.xxx <name-of-the-control-input-file>
```

The program will generate a screen output (you might want to redirect it to disk using standard redirection rules) and also other optional output files which will be placed in the new subdirectory with the name specified in the title section of the control input file.

Chapter 4

Structure of the DATA Files

4.1 Control Input File

4.1.1 General structure

The control input file consists of blocks separated by empty lines. Each block contains the control information for a particular job. The program reads blocks sequentially and terminates when it finds the word tw END in the beginning (first three positions) of the block. All the lines in the control input file must be not longer than 80 symbols. The symbols after first 80 are ignored.

Each block consists of three sections:

1. TITLE SECTION (one line) - the title of the job and optionally the keyword specifiyng the name of the job. This keyword has the following format: `JOBNAME=<name-of-the-job>`. If this keyword is specified the program will create a subdirectory `name-of-the-job` for optional output files. Otherwise a subdirectory with the standard name (consequtive number of the job) will be created.

2. COMMENT SECTION (one line) - any text specifying the current job

3. KEYWORDS SECTION (as many lines as you want but the total number of symbols should not exceed 480) - the keywords controlling the job. The detailed description of all the keywords and related options is given in the next subsection.

4.1.2 Keywords

There are two types of keywords in the PCET 2.0 program. The keywords of the first type set some global controls for the job and are mandatory. The keywords of the second type provide the control information about specific tasks which should be performed. Usually these keywords require mandatory set of options given in brackets. The format for the first type of keywords is (no spaces before or after "="!)

```
KEYWORD=<value>
```

The format for the second type is (no spaces before the opening bracket!)

```
KEYWORD(Option1,Option2,Option3,...)
```

The keywords are case-insensitive and should be separated by spaces. The options are separated by commas and are case-insensitive as well.

Below is the list of keywords with detailed descriptions.

METHOD=N

Sets the method of calculation of mixed electronic/vibrational states for all the tasks in the current job.

N=**1** - using the DIABATIC approach: diagonalization of the total Hamiltonian in the basis of the products of DIABATIC electronic states (EVB) and vibrational states (in the DIABATIC EVB potentials).

N=**2** - using the ADIABATIC approach: diagonalization of the total Hamiltonian in the basis of the products of ADIABATIC electronic states and vibrational states (in the ADIABATIC potentials). Note that this approach involves the calculation of non-adiabatic "d" and "g" derivative terms.

N=**3** - using the DOUBLE ADIABATIC approach: the non-adiabatic "d" and "g" derivative terms are assumed to be zero.

CHARGE=Q

Sets the total charge of the solute Q (a.u.).

QUANTUM(*Options***)**

Defines parameters for the quantum subsystem. The available options are:

`PROTON` - the quantum particle is proton

`DEITERIUM` - the quantum particle is deiterium

`MASS=<m>` - mass of the quantum particle (a.u.)

`NGRID=`N - number of grid points along the coordinate of quantum particle (must be a power of two). Default is 128.

`NGRIDS=`N - number of grid points along the coordinate of quantum particle for solvation calculations (must be a power of two and smaller than NGRID). Default is NGRID. If `NGRIDS=0` then solvation calculations are done only at one single point in the middle of the PT interface.

`LIMITS=`A/B - left (A) and right (B) integration limits for one-dimensional Schrödinger equation (Å).

`NPRST=`N - number of proton vibrational states to include. Default is 40.

GATING(*Options***)**

Defines parameters for the gating mode. The available options are:

`DMASS=<m>` - mass of the proton donor (proton units)

`AMASS=<m>` - mass of the proton acceptor (proton units)

`NGRID=`N - number of grid points along the gating coordinate (must be a power of two). Default is 1 (input geometry only).

`NGRIDS=`N - number of grid points along the gating coordinate for solvation calculations (must be a power of two and smaller than NGRID). Default is NGRID. If `NGRIDS=0` then solvation calculations are done only at one single point in the middle of the PT interface.

`LIMITS=`A/B - left (A) and right (B) integration limits for one-dimensional Schrödinger equation (Å).

`NGAST=`N - number of vibrational states to include for gating coordinate. Default is 10.

`QUANTUM` - flag for quantization along the gating coordinate.

HGAS(*Options*)

Defines parameters of the gas phase potential. The available options are:

`MM5` - EVB potential with standard MM parameterization for five-site Nocera-like systems.

`LEPS5` - 2D LEPS EVB potential for five-site models.

`WATER` - Voth-Schmitt MS-EVB potential for water clusters. The parameters are in the include file `msevbpar.inc`.

`PARS=<file>` - the parameters for the potential are given in the external file `<file>` (the format of the file is described in the next section).

`DIST_ET=`d_{ET} - electron transfer distance (Å) (meaningful only for WATER potential)

`DIST_PT=`d_{PT} - proton transfer distance (Å) (meaningful only for WATER potential)

`DELTAG=`ΔE^0 - energy bias for ET states (kcal/mol) (meaningful only for WATER potential)

`VEPTMETH=`N - defines mixed coupling between EVB states (meaningful only for WATER potential)

`GEOM=<file>` - the geometry and EVB charges are given in the external file `<file>` (the format of the file is described in the next section).

`XYZOUT=<file>` - the cartesian coordinates are written to the external file `<file>` in XYZ format.

SOLV(*Options*)

Defines the model and parameters for solvation calculations. The available option are:

`WATER` - the solvent is water

`H2O` - the solvent is water

`CH2CL2` - the solvent is methylene chloride (dichloromethane)

`MEOH` - the solvent is methanol

`ETOH` - the solvent is ethanol

`CH3CN` - the solvent is CH_3CN

`DCE` - the solvent is DCE

`THF` - the solvent is THF (tetrahydrofurane)

`NBZ` - the solvent is nitrobenzene

`DMF` - the solvent is DMF

`EPS0`=ϵ_0 - static dielectric constant

`EPS8`=ϵ_∞ - optical (electronic) dielectric constant

`ELLIPSE` - simple electrostatic ellipsoidal model will be used

`A`=a - major semiaxis of the ellipsoidal cavity

`B`=b - minor semiaxis of the ellipsoidal cavity

`FRCM` - advanced FRCM model will be used

`KAPPA`=κ - factor for VdW radii

`DELTA`=δ - thickness of the inner layer in FRCM

`GEOM=<file>` - the geometry and EVB charges are given in the external file `<file>` (the format of the file is described in the next section).

`TREAD=<file>` - the reorganization energy matrices on the grid are read from external binary file `<file>` saved in previous calculation.

`TWRITE=<file>` - the reorganization energy matrices on the grid are saved in the external binary file `<file>`.

`XYZOUT=<file>` - the cartesian coordinates are written to the external file `<file>` in XYZ format.

`NOSYMD` - the reorganization energy martices are not about the diagonal from top left to bottom right. This keyword should only be used to check how good the approach is working. By default the reorganization energy matrices will be symmetrized. (See solint.f and tmat.f)

`SYMT` - the solvent reorganization energy martices are symmetrized so that the properties for a symmetric PCET system are correctly reproduced.

`SYMET` - the solvent reorganization energy martices are symmetrized so that the properties for a symmetric ET system are correctly reproduced. (NOTE, this should only be used with the ET2 keyword.

`SYMPT` - the solvent reorganization energy martices are symmetrized so that the properties for a symmetric PT system are correctly reproduced. (NOTE, this should only be used with the PT2 keyword.

`REDDENS` - All the elements of the solvent reorganization energy martices which depend on 2b are obtained from all the other elements depending only on 1a,1b,2a. This should always be true anyway. A system for which this is not true has some major problems and should be used with caution. This keyword can also be used when the charges for the 2b state for solvation are not obtainable. (simply put in any charges that are not all zero and such that the column has at least one different element from the other columns:1a,1b,and 2a.)

PTGAS=`<file>`

The gas-phase and electronically solvated energy profiles along the proton coordinate are written to the external file `<file>` (default filename if `ptgas`).

PTSOL(*Options*)

The solvated energy profiles along the proton coordinate are written to the external file `<file>` (default filename if `ptsol`). The available options are:

`ZP=`z_p - value of the PT solvent coordinate

`ZE=`z_e - value of the ET solvent coordinate

`OUTPUT=<file>` - the name of the output file

ET2(*Options*)

Calculates one-dimensional free energy curves and nonadiabatic rate for a single ET reaction between specified EVB states. The gating (PT donor-acceptor) distance is fixed at the value specified in the gas-phase geometry input file. The available options are:

`XP=<XP>` - x coordinate of the proton (it is assumed that the PT interface is linear and aligned along the x-axis, and the origin is at the center of mass of the PT interface). If `XP` option is not specified then the location of the proton is taken from the gas phase geometry input file.

REAC=<N> - the EVB state N (1/2/3/4) will be considered as a reactant state in the ET reaction. If this option is not specified then the state 1 (1a) is assumed to be the reactant state.

PROD=<M> - the EVB state M (1/2/3/4) will be considered as a product state in the ET reaction. If this option is not specified then the state 3 (2a) is assumed to be the product state.

ZE1=<ZE1> - the left limit on the grid along the solvent coordinate z_e (kcal/mol). The default is $-3\lambda_{ET}$, where λ_{ET} is the ET reorganization energy.

ZE2=<ZE2> - the right limit on the grid along the solvent coordinate z_e (kcal/mol). The default is $+3\lambda_{ET}$, where λ_{ET} is the reorganization energy.

NZE=<N> - number of points along the grid. The default is 100.

PLOT=<filename> - name of the output file with the free energy profiles (the default filename is et.dat).

RATE=<T> - the nonadiabatic rate at $T =$<T> K will be calculated. The default temperature is 298.15 K.

PT2(*Options*) (**NOT ACTIVATED IN THE CURRENT VERSION!**

Calculates one-dimensional free energy curves for a single PT reaction between the EVB states 1a and 1b. The available options are:

ADIAB - calculate adiabatic electron/proton vibrational states

DIABA - calculate diabatic states (two output files)

ZP1=<zp1> - the left limit on the grid along the solvent coordinate z_p (kcal/mol). The default is $-2\lambda_{ET}$, where λ_{PT} is the reorganization energy.

ZP2=<zp2> - the right limit on the grid along the solvent coordinate z_p (kcal/mol). The default is $+2\lambda_{PT}$, where λ_{PT} is the reorganization energy.

NZP=<N> - number of points along the grid. The default is 100.

NSTATES=N - number of states to plot

PLOT=<filename> - name of the output file with the free energy profiles (the default filename is pt.dat).

`WEIGHTS=<file>` - calculate EVB weights for `NSTATES` states and write it to the external file `<file>` (default filename `pt-weights.dat`)

Note: the PT reactant and product EVB states are 1a and 1b (first and second EVB states defined in input data. The charges for 2a and 2b states are not relevant in this type of calculation, but in order to allow further calculations for PCET reaction the charges for 2a state (third state) must differ from charges for 1b state (second state). Otherwise the program will issue a message that truncated reorganization energy matrix is singular and the job will be stopped.

SURF3(*Options***)**

Calculates the three-dimensional free energy surfaces on rectangular grid in the space of solvent coordinates z_p and z_e and the gating coordinate R. Output data are written to the specified external file in the format compatible with GNUPLOT plotting program. The available options are:

`ADIAB` - calculate adiabatic electron/proton vibrational free energy surfaces

`DIAB2` - calculate ET diabatic free energy surfaces (two output files)

`DIAB4` - calculate diabatic free energy surfaces (four output files)

`SCALE` - scale solvent coordinates with the reorganization energies

`ZP=`$z_{p1}/z_{p2}/N_p$ - grid along z_p: N_p points from z_{p1} to z_{p2}.

`ZE=`$z_{e1}/z_{e2}/N_e$ - grid along z_e: N_e points from z_{e1} to z_{e2}.

`NSTATES=`N - number of states to plot

`OUTPUT=<file>` - name of the output files with surface data (default filename `states`)

`WEIGHTS=<file>` - calculate EVB weights for `NSTATES` states and write it to the external file `<file>` (default filename `weights.grid`)

`DKLIN=<file>` - name of the input file with a specification of nonadiabatic couplings between adiabatic states (only for ADIAB)

`DKLOUT=<file>` - name of the output file with nonadiabatic couplings

PATH2(*Options*)

Calculates the free energy along the specified path in the space of solvent coordinates z_p and z_e. The gating coordinate SHOULD BE treated quantum-mechanically. Output data are written to the specified external file in the format compatible with the GNUPLOT plotting program. The available options are:

`ADIAB` - calculate adiabatic electron/proton vibrational free energy surfaces

`DIAB2` - calculate ET diabatic free energy surfaces (two output files)

`DIAB4` - calculate diabatic free energy surfaces (four output files)

`P1=`z_{p1}/z_{e1} - first point on the straight line path

`P2=`z_{p2}/z_{e2} - second point on the straight line path

`NPATH=`N - number of points along the straight line path (N/2...P1...N...P2...N/2)

`CURVE=<file>` - name of the files with path data

`NSTATES=`N - number of states to plot

`OUTPUT=<file>` - name of the output files with surface data (default filename `states.path`)

`WEIGHTS=<file>` - calculate EVB weights for `NSTATES` states and write it to the external file `<file>` (default filename `weights.path`)

`DKLIN=<file>` - name of the input file with a specification of nonadiabatic couplings between adiabatic states (only for ADIAB)

`DKLOUT=<file>` - name of the output file with nonadiabatic couplings

MIN2(*Options*)

Sets parameters for the routine which finds minima on the spesified two-dimensional free energy surface (gating coordinate is quantized!) using canonical Newton-Raphson minimization algorithm. The available options are:

`ADIAB=`N - search on the N-th adiabatic free energy surface

`DIAB2=`N/M - search on the N-th ET diabatic surface within M-th set. M must be either 1 (1a/1b) or 2 (2a/2b).

DIAB4=N/M - search on the N-th ET/PT diabatic surface within M-th set. M can be 1 (1a), 2 (1b) 3 (2a) or 4 (2b).

ZP0=<VALUE>/<SCALE> - initial approximation for z_p coordinate and a scaling factor. Scaling factor is intended to equalize the scales for both coordinates, sometimes it makes life easier for the minimization procedure)

ZE0=<VALUE>/<SCALE> - the same for z_e coordinate.

ACC=<VALUE> - the desired accuracy of the minimization

SLIM=<VALUE> - the maximum length of the Newton-Raphson step

MAXIT=N - maximum number of Newton-Raphson steps allowed

WEIGHTS - prints out the results of the wavefunction analysis to the standard output file

WEIGHTS=<filename> - prints out the results of the wavefunction analysis to the external file

WAVEFUN=<filename> - dump the proton vibrational wavefunctions to the external file ¡filename¿

WAVEFUN2(*Options*)

Calculates and writes out vibrational wavefunctions (proton and gating) and potential energy profiles at specified values of solvent coordinates to the external file. The available option are:

ZP=<VALUE> - value of the solvent coordinate z_p

ZE=<VALUE> - value of the solvent coordinate z_e

ADIAB - adiabatic electron/proton vibrational free energy surfaces

DIAB2=<ISET> - ET diabatic free energy surfaces. ISET is either 1 or 2.

DIAB4=<ISET> - diabatic free energy surfaces ISET is either 1 or 2 or 3 or 4.

NVIBST - number of proton vibrational states to print

NGATST - number of gating vibrational states to print

OUTPUT=<filename> - name of the external output file

WAVEFUN3(*Options***)**

Calculates and writes out proton vibrational wavefunctions and potential energy profiles at specified values of solvent coordinates and on the grid along the gating coordinate to the external file. The available option are:

`ZP=<VALUE>` - value of the solvent coordinate z_p

`ZE=<VALUE>` - value of the solvent coordinate z_e

`ADIAB` - adiabatic electron/proton vibrational free energy surfaces

`DIAB2=<ISET>` - ET diabatic free energy surfaces. `ISET` is either 1 or 2.

`DIAB4=<ISET>` - diabatic free energy surfaces `ISET` is either 1 or 2 or 3 or 4.

`NVIBST` - number of proton vibrational states to print

`NGATST` - number of gating vibrational states to print

`OUTPUT=<filename>` - name of the external output file

RATE2(*Options***)**

Calculates the nonadiabatic rate of the PCET reaction with quantum treatment of the gating coordinate. The available options are:

`T=<value>` - absolute temperature in K

`PREC=`I - precursor state I is the only initial state. No Boltzmann averaging over the initial states is performed.

`NPREC=`N - N precursor states are taken into account. The total rate is averaged over initial precursor states with Boltzmann weights.

`NSUCC=`M - M successor states are taken into account

`ZPREC=`$z_p^{(R)}/z_e^{(R)}$ - guess for the reactant minimum on the precursor free energy surface (kcal/mol)

`ZSUCC=`$z_p^{(P)}/z_e^{(P)}$ - guess for the product minimum on the successor free energy surface (kcal/mol)

`ERANALY` - the reorganization free energy is evaluated analytically using the expression (55) from Ref.[3]. Otherwise (if not specified) it is evaluated numerically according to Marcus definition.

EANUMER - the activation free energy is evaluated numerically as the difference between the free energies at the intersection point and at the reactant minimum. Otherwise (if not specified) the activation free energy is evaluated analytically using the Marcus relation $E_a = (\Delta G^0 + \lambda)^2 / (4\lambda)$

WEIGHTS - total EVB weights are printed out for all minima and intersection points

LOG=<filename> - all output is written to the external file `filename`. If the LOG option is not specified the output is directed to the standard output (unit 6).

ACC=<VALUE> - the desired accuracy of the minimization during location of reactants and products minima (kcal/mol)

SLIM=<VALUE> - the maximum length of the Newton-Raphson step in the minimization (kcal/mol)

XACC=<VALUE> - the desired accuracy in the location of the crossing point between one-dimensional slices of the reactant and product free energy surfaces (kcal/mol)

MAXIT=N - maximum number of Newton-Raphson steps allowed

MAXITX=N - maximum number of steps in locating a crossing point

ZPS=<SCALE> - scaling factor for z_p coordinate in the minimization

ZES=<SCALE> - scaling factor for z_e coordinate in the minimization

RATE3(*Options*)

Calculates the nonadiabatic rate of the PCET reaction with classical equilibrium treatment of the gating coordinate. The available options are:

T=<value> - absolute temperature in K

PREC=I - precursor state I is the only initial state. No Boltzmann averaging over the initial states is performed.

NPREC=N - N precursor states are taken into account. The total rate is averaged over initial precursor states with Boltzmann weights.

NSUCC=M - M successor states are taken into account

`ZPREC=`$z_p^{(R)}$`/`$z_e^{(R)}$ - guess for the reactant minimum on the precursor free energy surface (kcal/mol)

`ZSUCC=`$z_p^{(P)}$`/`$z_e^{(P)}$ - guess for the product minimum on the successor free energy surface (kcal/mol)

`ERANALY` - the reorganization free energy is evaluated analytically using the expression (55) from Ref.[3]. Otherwise (if not specified) it is evaluated numerically according to Marcus definition.

`EANUMER` - the activation free energy is evaluated numerically as the difference between the free energies at the intersection point and at the reactant minimum. Otherwise (if not specified) the activation free energy is evaluated analytically using the Marcus relation $E_a = (\Delta G^0 + \lambda)^2/(4\lambda)$

`WEIGHTS` - total EVB weights are printed out for all minima and intersection points

`LOG=<filename>` - all output is written to the external file `filename`. If the `LOG` option is not specified the output is directed to the standard output (unit 6).

`ACC=<VALUE>` - the desired accuracy of the minimization during location of reactants and products minima (kcal/mol)

`SLIM=<VALUE>` - the maximum length of the Newton-Raphson step in the minimization (kcal/mol)

`XACC=<VALUE>` - the desired accuracy in the location of the crossing point between one-dimensional slices of the reactant and product free energy surfaces (kcal/mol)

`MAXIT=`N - maximum number of Newton-Raphson steps allowed

`MAXITX=`N - maximum number of steps in locating a crossing point

`ZPS=<SCALE>` - scaling factor for z_p coordinate in the minimization

`ZES=<SCALE>` - scaling factor for z_e coordinate in the minimization

`GRQUANT` - exact quantum distribution function for harmonic gating potential will be used

`GRQUANT` - classical (Boltzmann) distribution function for harmonic gating potential will be used

`VERBOSE` - verbose output (for each gating grid point).

`GMASS` - reduced mass for gating coordinate (Daltons)

`GFREQ` - harmonic frequancy for gating coordinate (1/cm)

`GAVER` - equilibrium gating distance (Angstrom)

4.2   Additional INPUT Files

4.2.1   Geometry and charges specification

This input file specifies the geometry and basis EVB point charge distributions for gas phase and solvation calculations. The format is universal, so you can specify either the same or different files in options for the HGAS and SOLV keywords. The examples are stored in the `work` subdirectory as files with `.gas` and `.sol` extensions.

Line 1: Keywords

One keyword is mandatory and defines the format for the geometry specification. You should specify either `XYZ` (cartesian coordinates) or tw `INT` (internal coordinates). If the file is intended for FRCM solvation calculations, you can also specify any FRCM keywords described in the FRCM manual.

Line 2 - Title

Any title specifying the geometry.

Line 3 - Comment

Any text related to geometry (can be empty).

Lines 4:N - Geometry specification

The geometry can be specified either in cartesian coordinates (`<element_symbol>` `<x> <y> <z>`) or in internal coordinates (`MOPAC` Z-matrix format). The allowed element symbols are H-No and also symbols 'De', 'Ae', 'Dp', 'Ap', 'Ps' for general electron donor, electron acceptor, proton donor, proton acceptor, and pseudoatom, respectively. Format is free and the section is terminated by an empty line.

Line N+2 - Title for charge distribution section

Any title specifying the EVB charges.

Line N+3:M - Charges for EVB states

Four columns in free format, the columns specify charges on atoms for EVB states 1a, 1b, 2a, and 2b, respectively. Note that the order of point charges should exactly correspond to the order of atoms in the geometry section. The input of charges is also terminated by an empty line.

Line M+2 - Title for PT interface

Any title specifying the PT interface.

Line M+3 - PT interface specification

Three numbers in free format identifying the proton donor, proton, and proton acceptor, respectively. The numbers are the ordering numbers of the atoms in the geometry specification.

Line M+4 - Title for ET interface

Any title specifying the ET interface.

Line M+5 - ET interface specification

Two numbers in free format identifying the electron donor and acceptor, respectively. The numbers are the ordering numbers of the atoms in the geometry specification.

4.2.2   Parameters for the MM5 gas phase potential

This input file contains the parameters for the gas phase EVB potential with standard MM parameterization. In can contain comment lines, empty lines and lines with parameters specifications. The comment lines must have 'C' or '#' in the first position. Empty lines are allowed anywhere and are just ignored by the reading routine. The parameters lines have the following structure:

```
 <Parameter name> <numerical value>
```

The names of the parameters are unique and are listed below (all dimensions are derivatives of kcal/mol and Å):

Morse parameters

`DNH` - N-H bond dissociation energy

`DOH` - O-H bond dissociation energy

`BNH` - N-H bond β parameter

`BOH` - O-H bond β parameter

`RNH` - N-H bond equilibrium distance

`ROH` - O-H bond equilibrium distance

Repulsion potential parameters `DRAH*EXP(-BRAH*RAH) + CRAH/RAH**9`

`DROH, BROH, CROH` - O-H bond

`DRNH, BRNH, CRNH` - N-H bond

Coulomb smoothing parameter

`KSI` - parameter in the exponent of the error function.

Constant correction terms (kcal/mol)

`CORR` - four values (one for each EVB state)

Proton coupling parameters `VPT0*EXP(-GAPT*(Q-QPT0))`

`VPT0_1, GAPT_1, QPT0_1` - for 1a-1b pair.

`VPT0_2, GAPT_2, QPT0_2` - for 2a-2b pair.

Electron coupling parameters `VET0*EXP(-GAET*(Q-QET0))`

`VET0_A, GAET_A, QET0_A` - for 1a-2a pair

`VET0_B, GAET_B, QET0_B` - for 1b-2b pair

Mixed coupling parameters `VETPT0*EXP(-GAETPT*(Q-QETPT0))`

`VETPT0_1, GAETPT_1, QETPT0_1` - for 1a-2b pair

`VETPT0_2, GAETPT_2, QETPT0_2` - for 1b-2a pair

4.2.3   Parameters for the LEPS5 gas phase potential

This input file contains the parameters for the gas phase EVB potential with LEPS parameterization. In can contain comment lines, empty lines and lines with parameters specifications. The comment lines must have 'C' or '#' in the first position. Empty lines are allowed anywhere and are just ignored by the reading routine. The parameters lines have the following structure:

```
<Parameter name> <numerical value>
```

The names of the parameters are unique and are listed below (all dimensions are derivatives of kcal/mol and Å):

Morse parameters

`DAH` - A-H bond dissociation energy (donor-hydrogen)

`DBH` - B-H bond dissociation energy (acceptor-hydrogen)

`DAB` - A-B bond dissociation energy (donor-acceptor)

`BAH` - A-H bond β parameter

`BBH` - B-H bond β parameter

`BAB` - A-B bond β parameter

`RAH` - A-H bond equilibrium distance

`RBH` - B-H bond equilibrium distance

`RAB` - A-B bond equilibrium distance

`RODd` - ET donor - PT donor equilibrium distance

`ROAa` - ET acceptor - PT acceptor equilibrium distance

Sato scaling parameters

`KAH` - A-H bond Sato parameter (donor-hydrogen)

`KBH` - B-H bond Sato parameter (acceptor-hydrogen)

`KAB` - A-B bond Sato parameter (donor-acceptor)

Overlap integral

 `SIGMA` - overlap integral between PT EVB states

Constant correction terms (kcal/mol)

 `CORR` - four values (one for each EVB state)

Electron coupling parameters `VET0*EXP(-BETA*RDA)`

 `VET0, BETA` - for 1a-2a and 1b-2b pairs

Harmonic force constants for ET-PT donor/acceptor bonds

 `KD1` - force constant for ET donor - PT donor bond in first ET state

 `KD2` - force constant for ET donor - PT donor bond in second ET state

 `KA1` - force constant for ET acceptor - PT acceptor bond in first ET state

 `KA2` - force constant for ET acceptor - PT acceptor bond in second ET
       state

4.2.4   Information for nonadiabatic couplings calculation

This input file lists the numbers of pairs of states between which to calculate
the nonadiabatic coupling vectors. The format is free. The first line contains
an integer N specifying the total number of pairs. The following lines contain
pairs of integers being the numbers of states.

4.3   OUTPUT Files

4.3.1   Standard output

Standard unit 6 is used for standard output throughout the program. You
can redirect the standard output to the disk file using standard redirection
rules for your operating system.

4.3.2   Geometry output

The program can produce the geometry files if the `XYZOUT` option is specified
with the `HGAS` or `SOLV` keywords. The files are written in standard "xyz"
format, so you can use any vizualization software to check the geometry (for
example, MOLDEN).

4.3.3 Surface2 data

The format of the files produced in surface calculations is compatible with the `GNUPLOT` plotting software. The order of columns is as follows:

z_p z_e $E_1(z_p, z_e)$ $E_2(z_p, z_e)$ $E_3(z_p, z_e)$ ... $E_{\mathrm{NSTATES}}(z_p, z_e)$

4.3.4 Surface3 data

The format of the files produced in surface calculations is compatible with the `GNUPLOT` plotting software. The order of columns is as follows:

z_p z_e R $E_1(z_p, z_e)$ $E_2(z_p, z_e)$ $E_3(z_p, z_e)$ ... $E_{\mathrm{NSTATES}}(z_p, z_e)$

4.3.5 PATH2 data

The format of the files produced in path calculations is compatible with almost any plotting software. The order of columns is as follows:

z_p z_e $E_1(z_p, z_e)$ $E_2(z_p, z_e)$ $E_3(z_p, z_e)$ ... $E_{\mathrm{NSTATES}}(z_p, z_e)$

4.3.6 Gas phase potential data

This output file is created if the `PTGAS` keyword is specified. The file contains the gas phase and electronically solvated 2D energy surfaces. The order of columns is as follows:

Column 1 - value of the proton coordinate

Column 2 - value of the gating coordinate

Columns 3:6 - gas phase diabatic energies

Columns 7:10 - gas phase adiabatic energies

Columns 11:14 - electronically solvated diabatic energies

Columns 15:18 - electronically solvated adiabatic energies

4.3.7 Solvated potential data

This output file is created if the `PTSOL` keyword is specified. The file contains the 2D solvated energy surfaces along the proton and gating coordinates. The order of columns is as follows:

Column 1 - value of the proton coordinate

Column 2 - value of the gating coordinate

Columns 3:6 - diabatic energies

Columns 7:10 - ET diabatic energies

Columns 11:14 - adiabatic energies

4.3.8 Vibrational wavefunctions data

WAVEFUN2 output files

Two output files are created if the `WAVEFUN2` keyword is specified.

The first file (with `.prot` extension) contains the proton vibrational wavefunctions on the gating coordinate grid. The order of columns is as follows:

Column 1 - value of the proton coordinate

Column 2 - value of the gating coordinate

Column 3 - electronic energy

Column 4 - double-adiabatic vibrational energy

Columns 5:NVIBST+5 - `NVIBST` vibrational wavefunctions scaled (x20) and shifted to the vibrational energy levels.

Columns NVIBST+6: - the same for the next electronic state

The second file (with `.gate` extension) contains the gating vibrational wavefunctions. The order of columns is as follows:

Column 1 - value of the gating coordinate

Column 2 - double-adiabatic proton vibrational energy

Column 3 - triple-adiabatic gating vibrational energy

Columns 4:NGATST+4 - NGATST vibrational wavefunctions scaled (x20) and shifted to the vibrational energy levels.

Columns NGATST+5: - the same for the next proton vibrational and electronic states

WAVEFUN3 output file

One output files is created if the WAVEFUN3 keyword is specified.

The file contains the proton vibrational wavefunctions on the gating coordinate grid. The order of columns is as follows:

Column 1 - value of the proton coordinate

Column 2 - value of the gating coordinate

Column 3 - electronic energy

Column 4 - double-adiabatic vibrational energy

Columns 5:NVIBST+5 - NVIBST vibrational wavefunctions scaled (x20) and shifted to the vibrational energy levels.

Columns NVIBST+6: - the same for the next electronic state

4.3.9 EVB weights

This output file is created if the WEIGHTS opiton is specified with the PATH or SURF keywords. The file contains the EVB weights of mixed electronic/vibrational states at each point along the path (or on the grid) in solvent space. The order of columns is as follows:

Column 1 - the value of z_p coordinate

Column 2 - the value of z_e coordinate

Column * - the value of the gating coordinate (only if SURF3)

Columns 3:6 - the EVB weights (in the order 1a,1b,2a,2b) for the ground state

Columns 7:10 - the EVB weights (in the order 1a,1b,2a,2b) for the first excited state

Columns 11:14 - the EVB weights (in the order 1a,1b,2a,2b) for the second excited state

etc.

4.3.10 Nonadiabatic couplings data

This output file is created if the `DKLIN` opiton is specified with the `PATH` or `SURF` keywords. The file contains the nonadiabatic coupling vectors between for pairs of states specified in the corresponding input file (see section about input files). The order of columns is as follows:

Column 1 - the value of z_p coordinate

Column 2 - the value of z_e coordinate

Column 3 - z_p-component of the coupling vector for the first pair of states

Column 4 - z_e-component of the coupling vector for the first pair of states

Column 5 - the length of the coupling vector for the first pair

Columns 6:8 - the same for the second pair of states

etc.

4.3.11 Nonadiabatic rates output

This file is created if the `LOG` opiton is specified with the `RATE` keyword. The file contains all the information concerning the nonadiabatic rate calculation.

Chapter 5

PCET Examples

The examples are stored in the `work` subdirectory and contain the input and output files.

5.1 Nocera systems

5.1.1 Nocera system 1: ellipsoidal model

5.1.2 Nocera system 1: FRCM model

5.1.3 Nocera system 2: ellipsoidal model

5.1.4 Nocera system 2: FRCM model

5.2 Model water systems

Chapter 6

List of subroutines and include files

6.1 Initialization and driving routines

main - the main program.

fes - calculates free energy of the particular mixed electronic/vibrational state (external function for **newton**.

fesmin - locates a minimum on the specified free energy surface.

feszz - calculates free energies of the mixed electronic/vibrational states and corresponding wavefunctions.

init - initializes constants, conversion factors and some common-blocks.

minima - driver for the searching a minimum on the specified free energy surface.

path - calculates free energy along the path in space of solvent coordinates

rate - calculates nonadiabatic PCET rate

setjob - sets parameters for the current job

setmat - driver for the calculation of the matrices (gas phase Hamiltonian matrix, reorganization energy matrices, first and second derivatives) on the grid

setmm1 - sets parameters for MM1 gas phase potential

surface - calculates free energy on the grid in space of solvent coordinates

tmat - calculates reorganization energy matrix

ugas - calculates gas phase potential energy

usol - calculates classical free energy

wavef - driver for calculation of the vibrational wavefunctions for output

weight - driver for calculation of the EVB weights

6.2 Geometry related routines

convrt - converts internal coordinates to cartesian

geoin - reads geometry from the input file

geoput - prints geometry in Z-matrix format

getchr - reads charge distributions for EVB states

getcoo - reads coordinates

rotate - rotates the molecule

straight - checks if three given atoms are aligned

6.3 MM1 gas phase potential related routines

d2h0mat - calculates second derivative of the gas phase Hamiltonian

dh0mat - calculates first derivative of the gas phase Hamiltonian

h0mat - calculates gas phase Hamiltonian matrix

6.4 Voth-Schmitt gas phase potential related routines

coulombic -

distance -

evbwei -

hiievb -

hijevb -

initevb -

msevb -

partial -

6.5   Routines working with character strings

clnopt - cleans extracted options string

digit - converts numeric field to double precision number

getopt - extracts options from the keyword

locase - converts string to lower case

nblen - calculates the length of the character string

read0 - reads control input file

reada - converts numeric fields to double precision numbers

rmdbsp - removes double spaces and forbidden symbols from the character string

rmsp - removes all spaces from the character string

upcase - converts string to upper case

wrtkey - prints out all specified keywords

6.6   Output related routines

printb - prints banner

prmatr - prints out a matrix

prngas - writes out the gas phase energy profiles

prnsol - writes out the solvated energy profiles

wfnprt - writes out the vibrational wavefunctions

xyzout - writes out the geometry in xyz format.

6.7   Ellipsoidal model related routines

bcoef - calculates the B_n coefficients in the expansion of the polarization potential in the ellipsoidal model

d2bcoef - calculates the second derivative of the B_n coefficients

dbcoef - calculates the first derivative of the B_n coefficients

d2polpot - calculates the second derivative of the polarization potential

d2tinfm - calculates the second derivative of the electronic reorganization energy matrix

dpolpot - calculates the first derivative of the polarization potential

dtinfm - calculates the first derivative of the electronic reorganization energy matrix

dtm - calculates the first derivative of the inertial reorganization energy matrix

plgndr - Legendre polynome of the first kind

polpot - calculates polarization potential

qlgndr - Legendre polynome of the second kind

selfen - calculates the self energy

6.8   FRCM related routines

conn

connudt

frcmdr

frcminit

getrad

getsfe

gettxt

mertu

modfe

myword

normch

prshor

rtsec

sealin

secexl

secins

secneb

secres

secsor

secteg

sfera1t

sfera3t

sfert0

sfert1

sfert2

solint

volmin

volsqu

6.9 Routines related to 1D Schrödinger equation

calcham - forms Hamiltonian for the 1D Schrödinger equation

calcwf - calculates proton vibrational wavefunction

four1 - fast Fourier transform routine

griddx - calculates the matrix of the first derivative

gridke - calculates the kinetic energy matrix

6.10 Miscellaneous utility routines

bubbli - sorts an array in descending order

calcdij - calculates the d_{ij} nonadiabatic coupling terms

calcgij - calculates the g_{ij} nonadiabatic coupling terms

crossp - locates a crossing point between two surfaces (along a straight line connecting two minima)

eispack - diagonalization routines

mxcopy - copies one matrix to another

newton - Neton-Raphson minimization routine

power2 - check if given integer is a power of two

primat - prints out a square matrix

prod - scalar product of two vectors

second - time routine (machine dependent!)

th - some character function

zcoup - calculates nonadiabatic coupling vectors with respect to the solvent coordinates

zero1 - sets all elements of the one-dimensional array to zero

zero2 - sets all elements of the two-dimensional array to zero

zero3 - sets all elements of the three-dimensional array to zero

6.11   Include files

SIZES - array dimensions for FRCM routines

SPHSIZES - array dimensions for FRCM routines

control.h - control flags

cst.h - constants and conversion factors

elmnts.h - symbols of chemical elements

gasmat.h - gas phase Hamiltonian matrices on the grid

geogas.h - gas phase geometry

geosol.h - geometry for solvation calculations

keys.h - keywords

pardim.h - array dimensions

parmm1.h - MM1 parameters

parsol.h - solvation quantities

quant.h - quantum subsystem parameters

solmat.h - reorganization energy matrices on the grid

evbato.inc -

evbham.inc -

msevbpar.inc - Voth-Schmitt EVB parameters for water

partial.inc -

waterpar.inc -

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