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Diabatic States from Nodal Structure Conservation

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For a Hamiltonian $H(\mathbf{q})$, given in a suitable set of basis states, we construct diabatic states from requiring conservation of their nodal structure. The diabatic states and energies are single-valued functions for an arbitrary number of parameters $\mathbf{q} \equiv \{q_1, q_2, \ldots, q_f\}$. The method is illustrated for nucleons moving in a deformed Woods-Saxon potential.

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Many-body systems like nucleons in nuclei and electrons in atoms, molecules, and clusters are basically described in the single-particle approximation, where the particles (or quasiparticles) move independently in a (self-consistent) mean potential V. The mean potential $V(\mathbf{q})$ depends on parameters $\mathbf{q} \equiv \{q_1, q_2, \ldots, q_f\}$ which denote, e.g., deformation degrees of a nucleus or cluster, the coordinates of nuclei in a molecule, or the strengths of external fields acting on the many-body system. The eigenstates $|\alpha(\mathbf{q})\rangle$ and eigenvalues $e_\alpha(\mathbf{q})$ of the Hamiltonian $H(\mathbf{q}) = T + V(\mathbf{q})$ define the adiabatic basis. Problems arise when the Schrödinger equation is solved for a time-dependent potential $V(\mathbf{q}(t))$. Only for small enough velocities $\dot{\mathbf{q}}(t)$, the particles follow the time-dependent potential adiabatically, i.e., along the adiabatic states (Born-Oppenheimer approximation). With increasing velocities $\dot{\mathbf{q}}(t)$, however, the particle motion deviates more and more from adiabaticity, the deviation being caused essentially by the derivative coupling $\langle\alpha(\mathbf{q})|\nabla_{\mathbf{q}}|\alpha'(\mathbf{q})\rangle$. In fact, near points where two adiabatic states come close (quasicrossing), the derivative coupling becomes large, because the (nodal) structures of the wave functions change rapidly.

The elimination of the derivative coupling within a subset of adiabatic states defines diabatic states which are smooth as function of $\mathbf{q}$. This transformation replaces the quasicrossings of adiabatic levels by corresponding crossings of diabatic levels, and hence such diabatic states form a more convenient basis for treating the time-dependent Schrödinger equation for $V(\mathbf{q}(t))$. A variety of construction methods for diabatic states has been introduced [1,2], e.g., by diagonalization of the derivative couplings [3,4] or—starting from some initial point in $\mathbf{q}$ space—by revealing the diabatic states from integration [5] or overlap projection [6]. A combination of overlap projection and diagonalization has been applied as rediagonalization method for fast rotating nuclei [7].

All these methods are perfect for systems, where different quasicrossings of adiabatic states are well separated. However, in situations where quasicrossings mix with each other, they become numerically difficult or unreliable. Stable diagonalization procedures can be used if it is possible to eliminate parts of the Hamiltonian $H(\mathbf{q})$, which are responsible for the repulsions in quasicrossings of adiabatic states, like symmetry-breaking terms for the mean field [8] or residual interactions between many-body configurations [6]. However, such procedures are limited to special problems.

In the following, we introduce a novel method which is based on stable diagonalization procedures for a Hamiltonian $H(\mathbf{q})$ given by its matrix elements in a suitable set of basis states. For the diabatic states $|\nu(\mathbf{q})\rangle$ we require (1) that they are *eigenstates of a diabatic Hamiltonian* $H_d(\mathbf{q})$, which is uniquely defined in $\mathbf{q}$ space, and (2) that they *conserve their nodal structure* while following the variation of $H(\mathbf{q})$ in an optimal way. The first requirement is basic to assure one-valued single-particle energies (i.e., potentials) $e_\nu(\mathbf{q})$ and states $|\nu(\mathbf{q})\rangle$ as functions of $\mathbf{q}$. The second requirement is crucial for diabaticity and, satisfying this via a variational principle involving $H(\mathbf{q})$ as described below, renders uniqueness to the definition of diabatic states.

The nodal structure of the wave functions in configuration space $\mathbf{r} \equiv \{x, y, z\}$ is associated with the kinetic energy operator T. Its separability $T = T_x + T_y + T_z$ suggests to determine the diabatic states as product states $|\nu\rangle = |\nu_x)|\nu_y)|\nu_z)$. Here we denote by $|\nu_i)$ the states in the separate subspaces $i = x, y$ or z, which build the Hilbert space vectors $|\nu\rangle$. If for a certain potential $V(\mathbf{q})$ any of the symmetry properties with respect to rotation, parity, and reflection (approximately) applies, the degree of separability may be reduced. For example, in case of axial symmetry of $V(\mathbf{q})$, $T = T_{\rho\phi} + T_z$, and hence $|\nu\rangle = |\nu_{\rho\phi})|\nu_z)$, where ρ, ϕ, z denote cylindrical coordinates.

In the following formulation we consider a twofold separability, i.e.,

$$|\nu(\mathbf{q})\rangle \equiv |\nu_1(\mathbf{q}))|\nu_2(\mathbf{q})). \tag{1}$$

Generalization to arbitrary separability is straightforward. Modifications for spin-1/2 particles are discussed below. In analogy to the definition of the adiabatic states from the variational principle $\delta\Sigma_\alpha\langle\alpha|H(\mathbf{q}) - \lambda|\alpha\rangle = 0$, we define the diabatic states (1) from

$$\delta\sum_{\nu_1\nu_2}\langle\nu_1\nu_2|H(\mathbf{q}) - \lambda|\nu_1\nu_2\rangle = 0 \tag{2}$$

with some upper limits in the summation as specified below. Introducing the expansion $|\nu_i) = \Sigma_{n_i}|n_i)(n_i|\nu_i)$ in terms of basis states $|n_i)$ in the two subspaces i and performing the variation with respect to $(n_i|\nu_i)$, we obtain the eigenvalue equations

$$\sum_{n_i'}[(n_i|h_i(\mathbf{q})|n_i') - \lambda_i \delta_{n_i n_i'}](n_i'|\nu_i) = 0 \qquad (3)$$

for the determination of eigenvalues λ_{ν_i} and expansion coefficients $(n_i|\nu_i)$. The Hamiltonians $h_i(\mathbf{q})$ are determined by averages from the original Hamiltonian $H(\mathbf{q})$,

$$h_i(\mathbf{q}) = \overline{(\nu_j|H|\nu_j)} = \frac{1}{N_j}\sum_{\nu_j=1}^{N_j}(\nu_j|H|\nu_j) \qquad (4)$$

with $i \neq j$ and N_j denoting the number of the lowest states in energy, which are used for averaging. The diabatic states $|\nu_i)$ are expected to depend only weakly on $N_j \gg 1$. Reasons are (i) that the separable part H_i of H remains unchanged while H_j yield only total energy shifts in h_i, and (ii) that the remaining coupling enters into h_i after averaging over the mean densities of all N_j states $|\nu_j)$. This average density depends only weakly on the number N_j. Furthermore, an overall scaling of the matrix elements of h_i by some factor would not affect the determination of $|\nu_i)$ from (3). For a global optimization we choose N_i equal to the number of diabatic states $|\nu_i)$, which are needed for obtaining accurate adiabatic states up to a given energy. Alternatively, one may choose to average over a subset of states which, e.g., are involved in certain crossings. This may lead to a better optimization locally.

Equations (3) and (4) have to be solved iteratively for $|\nu_i)$ starting, e.g., with the basis states $|n_i)$. Finally, the diabatic energies e_ν are defined as the expectation values of $H(\mathbf{q})$ in the diabatic states $|\nu(\mathbf{q})\rangle$, and hence the diabatic Hamiltonian H_d is given by

$$H_d(\mathbf{q}) = \sum_\nu |\nu\rangle e_\nu \langle\nu| \quad \text{with} \quad e_\nu(\mathbf{q}) \equiv \langle\nu|H|\nu\rangle. \qquad (5)$$

Note that $H_d(\mathbf{q}) \neq h_1(\mathbf{q}) + h_2(\mathbf{q})$.

With this method (1)–(5) we have identified the interaction $H - H_d$ between the diabatic states, which causes the repulsion between the adiabatic energies. The derivative coupling

$$\langle\nu|\nabla_{\mathbf{q}}|\nu'\rangle = (\nu_1|\nabla_{\mathbf{q}}|\nu_1')\delta_{\nu_2\nu_2'} + (\nu_2|\nabla_{\mathbf{q}}|\nu_2')\delta_{\nu_1\nu_1'} \qquad (6)$$

vanishes between most diabatic states ν and ν'. Some smooth and small couplings exist only between states which differ either in ν_1 or in ν_2, and hence, which never cross in energy. This part of the derivative coupling is not removable in our method.

The degree of mixing in the unitary transformation $|\nu\rangle = \Sigma_\alpha|\alpha\rangle\langle\alpha|\nu\rangle$ between diabatic and adiabatic states can be characterized by the spreading width

$$\Gamma_\nu = 2\sqrt{\sum_\alpha (e_\nu - e_\alpha)^2 |\langle\alpha|\nu\rangle|^2} \qquad (7)$$

of a diabatic state ν over the adiabatic states. It should be noted that e_ν is according to (5) equal to the mean value $\Sigma_\alpha e_\alpha |\langle\alpha|\nu\rangle|^2$. For a Lorentzian shape of $|\langle\alpha|\nu\rangle|^2$ and a dense spectrum, Γ_ν is the full width at half maximum of the distribution. If Γ_ν is on average small compared to the mean level spacing D, i.e., $\overline{\Gamma_\nu} \ll D$, the diabatic states are essentially only pairwise mixed near crossings, such that the adiabatic energies exhibit just distant quasicrossing. In the strong-coupling limit $\overline{\Gamma_\nu} > D$ the diabatic states are spread over many adiabatic states, such that practically all quasicrossings are mixed. As known from the study of chaotic spectra [9] this transition from weak to strong coupling is rather rapid as function of $\overline{\Gamma_\nu}/D$.

In the following we illustrate the construction and properties of global (i.e., globally optimized) diabatic states for the deformed nucleus with 90 protons and 134 neutrons (^{225}Th), which is described by a Woods-Saxon potential [10] with axial and left-right symmetry. As function of the parameter ϵ the deformation varies from oblate via spherical to prolate shapes as indicated along the axis in Fig. 1. There exist good quantum numbers: m for the projection j_z of the total angular momentum $\mathbf{j}$ along the symmetry axis (z axis) of the nucleus, and π for the parity operator P. Therefore, the matrix of the Hamiltonian H consists of uncoupled blocks $m\pi$. Since the spin-orbit interaction is strong in nuclei the diabatic states are considered in the form

$$|\nu_{m\pi}\rangle = \sum_{m_s}|\nu_\rho, m_l = m - m_s)|\nu_z)|m_s), \qquad (8)$$

where m_l, m_s denote the projection of angular momentum and spin along the z axis. The parity of $|\nu_z)$ is given by $\pi(-1)^{m_l}$. For weak spin-orbit interactions (like in atoms

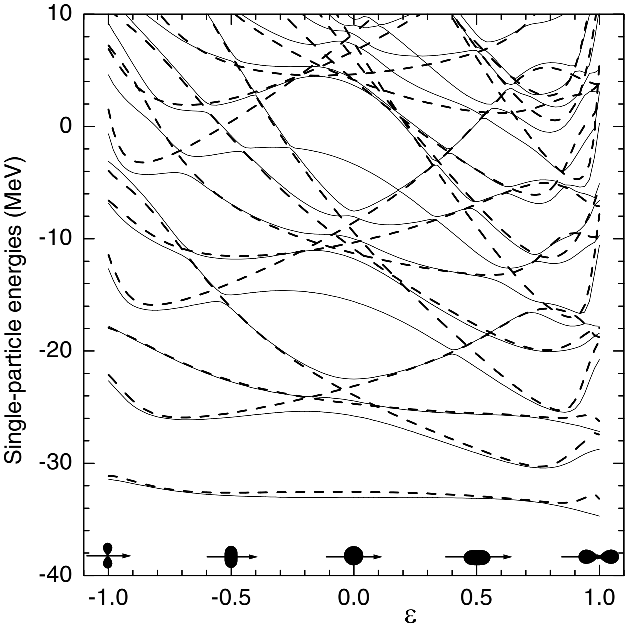

FIG. 1. Adiabatic (solid lines) and diabatic (dashed lines) proton levels with $m\pi = 1/2+$ as functions of deformation for ^{224}Th.

and molecules) m_l and m_s should be considered as independent in the definition of diabatic states, and hence $|\nu, \text{weak}\rangle = |\nu_\rho m_l)|\nu_z)|m_s)$. Continuing with the strong-coupling limit (8) we obtain for (4)

$$\begin{aligned} h^{\pi m_l}_{\rho\phi}(\epsilon) &= \overline{(\nu_z m_s|H|\nu_z m_s)}, \\ h^{\pi_z}_{z}(\epsilon) &= \overline{(\nu_\rho m_l; m_s|H|\nu_\rho m_l; m_s)}, \end{aligned} \tag{9}$$

where the averages are restricted by $(-1)^{m_l}\pi_z = \pi$ and $m_l + m_s = m$.

For the basis states $|n_\rho m_l)$ and $|n_z)$, i.e., deformed oscillator states in [10], the eigenvalue Eq. (3) reads

$$\begin{aligned} \sum_{n'_\rho}[(n_\rho|h^{\pi m_l}_{\rho\phi}|n'_\rho) - \lambda_{\rho\phi}\delta_{n_\rho n'_\rho}](n'_\rho|\nu_\rho) &= 0, \\ \sum_{n'_z}[(n_z|h^{\pi_z}_{z}|n'_z) - \lambda_{z}\delta_{n_z n'_z}](n'_z|\nu_z) &= 0 \end{aligned} \tag{10}$$

with fixed m_l and π_z, respectively. Finally, the diabatic Hamiltonian is defined by

$$H^{(m\pi)}_d = \sum_\nu |\nu_{m\pi}\rangle e^{(m\pi)}_\nu \langle \nu_{m\pi}| \tag{11}$$

with $e^{(m\pi)}_\nu \equiv \langle \nu_{m\pi}|H|\nu_{m\pi}\rangle$. Since no essential dependence of the diabatic levels on the number of averaging states has been observed here, we have used the trace over all states in (9).

The calculations are carried out in a rather broad range of deformations, i.e., from extreme oblate to extreme prolate shapes. Figure 1 shows the results for $m\pi = 1/2+$. In large parts of the diagram a remarkable correspondence between diabatic and adiabatic levels is observed. Differences are particularly large around $\epsilon = 0$ (spherical shape), which stem from the strong spin-orbit interaction.

Figure 2 illustrates the mixing of a diabatic state $|\nu, 1/2+\rangle$ into adiabatic states $|\alpha, 1/2+\rangle$ by the spreading width (7) averaged over the ν states with a Gaussian of standard deviation 5 MeV around the Fermi energy. As one can see from Fig. 2, the spreading width $\overline{\Gamma_\nu}$ is much larger than the average spacing of the adiabatic states. Thus, many adiabatic states (not just the two closest) contribute to a diabatic one (strong coupling).

To characterize the dependence of the wave functions on deformation, we consider the mass parameter in the cranking approximation,

$$M = \hbar^2 \sum_{\lambda\lambda'} \frac{p_\lambda - p_{\lambda'}}{e_{\lambda'} - e_\lambda} |\langle\lambda|\partial/\partial q|\lambda'\rangle|^2. \tag{12}$$

Here $\lambda = \alpha, \nu$ for adiabatic and diabatic motion, respectively. The single-particle occupation probabilities p_α, p_ν are given by Fermi functions for $T \approx 0$. The derivatives $\langle\nu|\partial/\partial q|\nu'\rangle$ are obtained by inserting (8), using the expansion in terms of the basis states $|n_\rho m_l)$ and $|n_z \pi_z)$, and taking the derivatives of (10).

The deformation dependence of the mass parameters is shown in Fig. 3. The rapid variations of the adiabatic states with deformation, in particular, around quasicrossings, are responsible for the large fluctuations in the adiabatic mass parameter. The smoothness of the diabatic states yields values which are 1 to 2 orders of magnitude smaller than the adiabatic values.

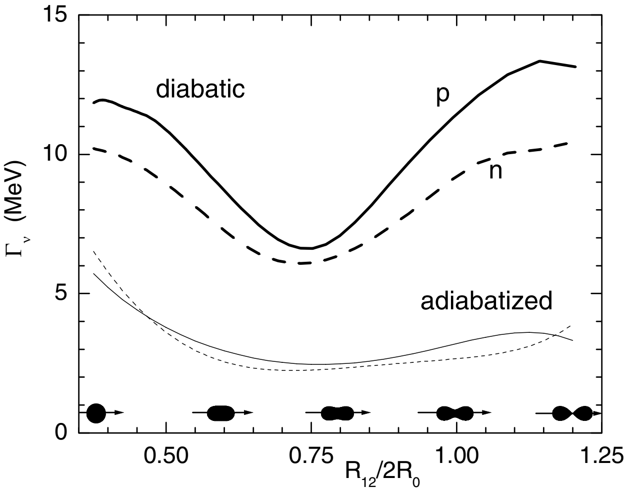

FIG. 2. The average spreading widths $\overline{\Gamma_\nu}$ of the diabatic proton (p) and neutron (n) states over the adiabatic states as functions of the distance R_{12} between the left and right centers of mass, $R_{12}/2R_0 \approx 0.375 + 0.286\epsilon + 0.500\epsilon^4$. The mean spreading widths obtained for the adiabatized diabatic states of Fig. 4 are given by the lower curves.

Our diabatic basis can be applied in various ways. For example, in certain time-dependent problems, one likes to know the diabatic motion starting at some initial deformation $\mathbf{q}_0$. This is simply accounted for by expanding the adiabatic states at $\mathbf{q}_0$ in terms of the diabatic states and

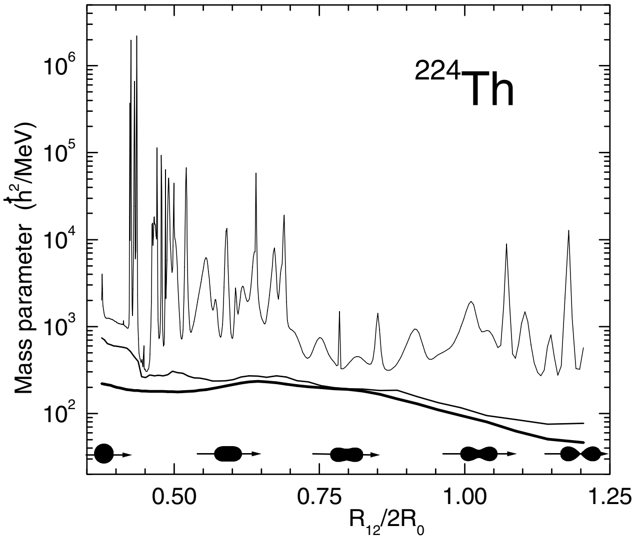

FIG. 3. The adiabatic (thin line) and diabatic (heavy line) mass parameters as functions of deformation. The line in between shows the mass parameter calculated for the adiabatized diabatic states $|\kappa\rangle$ illustrated in Fig. 4.

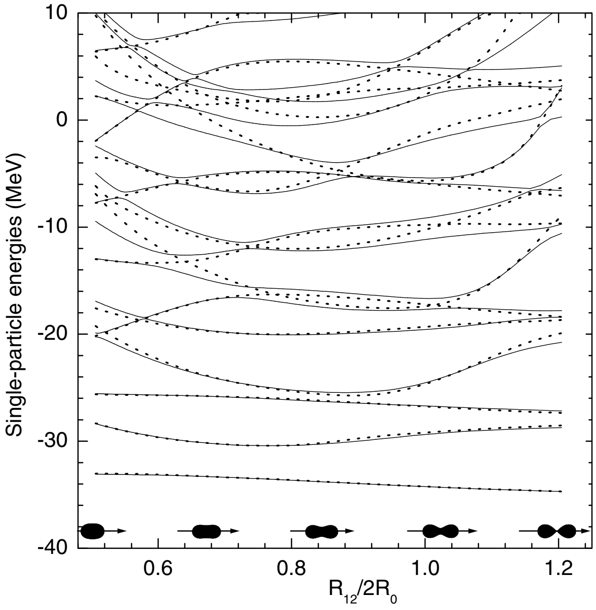

FIG. 4. The adiabatized diabatic levels (dotted lines) and the adiabatic energies (solid lines) as functions of deformation for the adiabatization parameters $\sigma = \sigma' = 3$ MeV.

keeping the expansion coefficients fixed for all **q** values (cf. [8]).

In other applications one is not interested in the diabatic states, but in approximations which lie in between the diabatic and the adiabatic limit. Such quasidiabatic states should keep the diabatic crossings, but approach adiabaticity with respect to states which are well separated in energy. To construct these quasidiabatic states, one can, for example, diabatize the adiabatic basis by removing the level repulsions with the help of the diabatic Hamiltonian (5).

Alternatively, starting from the diabatic basis, we also can construct quasidiabatic states by adiabatization in the following way. We introduce two steps of diagonalizations,

$$\begin{aligned} \mathrm{diag}\{e_\nu \delta_{\nu\nu'} + H_{\nu\nu'}(1 - F_{\nu\nu'})\} &\longrightarrow |k\rangle, \\ e_k \mathrm{diag}\{N_{kk'} F'_{kk'}\} &\longrightarrow |\kappa\rangle, \end{aligned} \tag{13}$$

where $F_{\nu\nu'}$, $F'_{kk'}$ are Gaussian cutoff factors in $e_\nu - e_{\nu'}$ and $e_k - e_{k'}$ with standard deviations σ and σ', respectively. The operator $N \equiv \Sigma_\nu |\nu\rangle \nu \langle \nu|$ is an artificial construct which is needed to remove the (small) repulsions created in the e_k's by the first diagonalization. Here we assume that the diabatic states ν are labeled by natural numbers $1, 2, \ldots$. Finally, the quasidiabatic energies are defined according to (5) by $e_\kappa = \langle \kappa | H | \kappa \rangle$. The result of this procedure is shown in Fig. 4. The quasidiabatic levels are much closer to the adiabatic ones than the diabatic levels. Still they are diabatic locally, i.e., near the crossings, where the quasidiabatic states are governed by some diabatic components. The mean spreading width of the adiabatized states $|\kappa\rangle$ is reduced considerably as illustrated in Fig. 2, while the mass parameter remains close to the diabatic one (Fig. 3). The discussion of further refinements of the method [e.g., averaging in (4) over different sets of diabatic states], or the description of diabatization procedures of adiabatic states are beyond the scope of this Letter and will be reported elsewhere.

In summary, we have introduced a novel method for the construction of diabatic states, which is based on the conservation of nodal structure. To a large extent these diabatic states are free from derivative couplings. Since only matrix elements of the Hamiltonian are needed, the method can be used in rather different (also self-consistent) approaches. The generalization to dissipative systems, which are described by complex (non-Hermitean) Hamiltonians (cf. [11–13]), is straightforward. Finally we conclude that our construction method of diabatic states can be successfully applied in many fields of chemistry and physics.

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