THE MULTI-CONFIGURATIONAL TIME-DEPENDENT HARTREE APPROACH

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Received 11 October 1989

A new multi-configurational approach to the time-dependent Schrödinger equation is proposed. This approach leads to working equations which are particularly simple and transparent. It can be used for n degrees of freedom and for any choice of the number of configurations. The new approach is tested on a model of coupled oscillators showing fast convergence towards the exact results as the number of configurations is increased.

1. Introduction

Approximate methods for solving molecular dynamics in a time-dependent picture have drawn increasing interest over the past decade [1–7]. For treating systems of several degrees of freedom the time-dependent Hartree (TDH) formalism [3,4] has been widely used. Beyond this single-configuration approach, work has been done on the time-dependent rotated Hartree (TDRH) formalism [7,8] and on the time-dependent multi-configurational approach [5,6,9] for solving the time-dependent Schrödinger equation. The latter work has so far been concentrated on the case of two degrees of freedom.

The known multi-configurational approaches [4,5,9] are based on the use of projection operators which – once for all times – assign different parts of the Hilbert space to different functions. For some problems [6] the choice of the projection operator is quite obvious, but for most cases it is not. For these cases it is unsatisfactory that the results explicitly depend on the choice of the projection operators.

It is the aim of this publication to present a new time-dependent multi-configurational approach which does not require the a priori introduction of projection operators. Our approach leads to working equations which are simpler and more transparent than those of the other approaches.

2. Outline of theory

2.1. General ansatz and working equations

We approximate the exact time-dependent wave function by the following multi-configurational trial function:

$$\Psi(x_1,\ldots,x_n,t)=\sum_{j_1=1}^{m_1}\cdots\sum_{j_n=1}^{m_n}a_{j_1\ldots j_n}(t)\times\phi_{j_1}^{(1)}(x_1,t)\ldots\phi_{j_n}^{(n)}(x_n,t)\,. \tag{1}$$

We emphasize that the numbers m_k of "single-particle" functions which build up the configurations can be chosen differently for each degree of freedom. However, each of these numbers should obey the condition $m_k^2\leqslant\prod_{l=1}^{n}m_l$. Otherwise our ansatz (1) will contain redundant configurations. Note that the case $n=2$ requires $m_1=m_2$.

The "single-particle" functions are assumed to be orthonormal at any time t,

$$\langle\phi_i^{(k)}|\phi_j^{(k)}\rangle=\delta_{ij}\,. \tag{2}$$

This requirement, however, does not make the representation (1) unique. Unitary transformations among the "single-particle" functions can be compensated by transforming the coefficients $a_{j_1\ldots j_n}$. The appearance of redundant parameters, on the other hand, allows us to additionally require

$$\langle\phi_i^{(k)}|\dot{\phi}_j^{(k)}\rangle=0\,. \tag{3}$$

0009-2614/90/$ 03.50

Here the dot denotes differentiation with respect to time. The constraint (3) ensures that the time evolution of Ψ is as much as possible performed by a change in the coefficients. Only the remaining part is accomplished by a change in the "single-particle" functions. The time derivative of the "single-particle" functions is thus minimized. Apart from this point of practical relevance the condition (3) simplifies the working equations.

Before continuing we have to introduce a notation which is suitable for the problem. We first define the multi-index J as a collection of all j_l except the kth one,

$$J=(j_1,\ldots,j_{k-1},j_{k+1},\ldots,j_n)\,. \tag{4}$$

In order to be unambiguously defined, J should carry the index k. However, to make the notation less clumsy, we rather prefer to label the quantity which carries the index J with a superscript k. We introduce the family of matrices $\mathbf{A}^{(k)}$,

$$A^{(k)}_{Jj}=a_{j_1\ldots j_{k-1}jj_{k+1}\ldots j_n} \tag{5}$$

and similarly the product wave function

$$\phi^{(k)}_J=\phi^{(1)}_{j_1}\ldots\phi^{(k-1)}_{j_{k-1}}\phi^{(k+1)}_{j_{k+1}}\ldots\phi^{(n)}_{j_n}\,. \tag{6}$$

Adopting the Dirac–Frenkel variational principle [10]

$$\langle\delta\Psi|\,\mathrm{i}\,\partial/\partial t-H|\Psi\rangle=0 \tag{7}$$

and using the conditions (2) and (3) one finds

$$\mathrm{i}\dot{a}_{j_1\ldots j_n}=\langle\phi^{(1)}_{j_1}\ldots\phi^{(n)}_{j_n}|H|\Psi\rangle \tag{8}$$

and

$$\sum_J A^{(k)*}_{Jj}\langle\phi^{(k)}_J|H|\Psi\rangle = \mathrm{i}\sum_I A^{(k)*}_{Ii}\sum_i\left(A^{(k)}_{Ii}\dot{\phi}^{(k)}_i+\dot{A}_{Ii}\phi_i\right). \tag{9}$$

In order to resolve the latter equation for $\dot{\phi}^{(k)}_j$ we define a matrix $\mathbf{B}^{(k)}$ by

$$\mathbf{B}^{(k)}=(\mathbf{A}^{(k)\dagger}\mathbf{A}^{(k)})^{-1}\mathbf{A}^{(k)\dagger}\,. \tag{10}$$

Note that the inversion is done in the small $m_k\times m_k$ space. Eq. (9) now becomes

$$\mathrm{i}\dot{\phi}^{(k)}_j=\sum_J B^{(k)}_{jJ}\left(\langle\phi^{(k)}_J|H|\Psi\rangle-\mathrm{i}\sum_I\dot{A}^{(k)}_{JI}\phi^{(k)}_I\right). \tag{11}$$

It is convenient to rewrite this equation by introducing the matrix of *mean-field* operators

$$\hat{H}^{(k)}_{IJ}=\langle\phi^{(k)}_I|H|\phi^{(k)}_J\rangle\,, \tag{12}$$

which operate only on the space $\{\phi^{(k)}_i(x_k)\}_{i=1,m_k}$. The caret indicates the operator nature of these quantities. Next we define the matrix elements

$$H_{i_1\ldots i_n,j_1\ldots j_n}=\langle\phi^{(1)}_{i_1}\ldots\phi^{(n)}_{i_n}|H|\phi^{(1)}_{j_1}\ldots\phi^{(n)}_{j_n}\rangle \tag{13}$$

and arrive alternatively to (8) and (11) at the equations

$$\mathrm{i}\dot{a}_{i_1\ldots i_n}=\sum_{j_1\ldots j_n}H_{i_1\ldots i_n,j_1\ldots j_n}a_{j_1\ldots j_n}\,, \tag{14}$$

$$\mathrm{i}\dot{\phi}^{(k)}_i=\sum_{J,j}B^{(k)}_{Ji}\left\{\hat{H}^{(k)}_{IJ}A^{(k)}_{Jj}-\mathrm{i}\delta_{IJ}\dot{A}^{(k)}_{Jj}\right\}\phi^{(k)}_j\,. \tag{15}$$

Depending on the implementation one may use either eqs. (8) and (11) or eqs. (14) and (15) as working equations. We shall call the method outlined above the multi-configurational time-dependent Hartree (MCTDH) approach.

2.2. Some relevant properties

It is illustrative to remove $\dot{\mathbf{A}}^{(K)}$ from eq. (15). With the aid of eqs. (5), (13) and (14) one arrives at

$$\mathrm{i}|\dot{\phi}^{(k)}_i\rangle=(\hat{1}-\hat{P}^{(k)})\sum_{IJj}B^{(k)}_{Ii}\hat{H}^{(k)}_{IJ}A^{(k)}_{Jj}|\phi^{(k)}_j\rangle\,, \tag{16}$$

where

$$\hat{P}^{(k)}=\sum_{l=1}^{m_k}|\phi^{(k)}_l\rangle\langle\phi^{(k)}_l| \tag{17}$$

denotes the (time-dependent!) projector on the space which is spanned by the "single-particle" functions of the kth degree of freedom. Eq. (16) proves that the propagation of the "single-particle" functions satisfies the constraint (3) (and hence eq. (2)) for all times – as it should.

Next we comment on the technical evaluation of the matrix $\mathbf{B}^{(k)}$. This matrix is just the More–Penrose pseudo-inverse [8,11,12] of $\mathbf{A}^{(k)}$. A numerical difficulty in evaluating $\mathbf{B}^{(k)}$ arises when $\mathbf{A}^{(k)\dagger}\mathbf{A}^{(k)}$ becomes singular. Such a singularity occurs when a smaller number of "single-particle" functions $\phi^{(k)}_j$ than m_k used in eq. (1) suffices to represent Ψ. To

avoid numerical difficulties we regularize [8] the (positive semi-definite) matrix $\mathbf{A}^{(k)\dagger}\mathbf{A}^{(k)}$ by adding $\epsilon\mathbf{1}$ to it, where ϵ denotes a small positive number (compare with section 3). The regularized pseudo-inverse is hence defined as

$$\mathbf{B}^{(k)} = (\mathbf{A}^{(k)\dagger}\mathbf{A}^{(k)} + \epsilon\mathbf{1})^{-1}\,\mathbf{A}^{(k)\dagger}\,. \tag{18}$$

An alternative way is to invert $\mathbf{A}^{(k)\dagger}\mathbf{A}^{(k)}$ by diagonalization and to regularize only those eigenvalues which are smaller than some threshold.

The eigenvalues of $\mathbf{A}^{(k)\dagger}\mathbf{A}^{(k)}$ provide an important diagnostic tool. Transforming the "single-particle" functions with the eigenvector matrix of $\mathbf{A}^{(k)\dagger}\mathbf{A}^{(k)}$ one obtains the so-called *natural* single-particle functions. The eigenvalues of $\mathbf{A}^{(k)\dagger}\mathbf{A}^{(k)}$ are the weights of the natural single-particle functions in the representation (1) as one can see from

$$\int |\Psi|^2 \,\mathrm{d}x_1 \ldots \mathrm{d}x_{k-1}\,\mathrm{d}x_{k+1} \ldots \mathrm{d}x_n = \sum_{ij} \phi_i^{*(k)}\,(\mathbf{A}^{(k)\dagger}\mathbf{A}^{(k)})_{ij}\phi_j^{(k)}\,.$$

A small eigenvalue shows that there is a natural function which hardly contributes. Hence a small eigenvalue signals convergence with respect to the number of "single-particle" functions of the kth degree of freedom. The eigenvalues add up to unity since trace $(\mathbf{A}^{(k)\dagger}\mathbf{A}^{(k)}) = \|\Psi\|^2 = 1$. We finally emphasize that the MCTDH propagation conserves both the norm and the mean energy.

2.3. Two degrees of freedom and connection to other work

For two degrees of freedom our ansatz (1) simplifies to

$$\Psi(x,y,t) = \sum_{i,j=1}^{m} a_{ij}(t)\,\phi_i(x,t)\,\chi_j(y,t)\,, \tag{19}$$

where we have used the symbols ϕ and χ rather than $\phi^{(1)}$ and $\phi^{(2)}$ for typographical simplicity. The coefficients now form a matrix $\mathbf{a}$ and one finds

$$\mathbf{A}^{(1)\mathrm{T}} = \mathbf{A}^{(2)} = \mathbf{a}\,, \tag{20a}$$

$$\mathbf{B}^{(1)\mathrm{T}} = \mathbf{B}^{(2)} = \mathbf{a}^{-1}\,, \tag{20b}$$

where, however, the last equality sign holds only when $\mathbf{a}^{-1}$ exists.

In order to make contact with the other multi-configuration approaches we first introduce the representation

$$\Psi(x,y,t) = \sum_{i=1}^{m} \tilde{\phi}_i(x,t)\,\tilde{\chi}_i(y,t)\,, \tag{21}$$

where $\{\tilde{\phi}_i\}$ and $\{\tilde{\chi}_i\}$ denote arbitrary sets (not necessarily orthogonal) of "single-particle" functions. By expansion of these "single-particle" functions in an orthonormal set one can show that the trial functions Ψ in eqs. (19) and (21) cover exactly the same trial space.

On the other hand one may "diagonalize" the presentation (19) by making use of the singular value decomposition [11] of $\mathbf{a}$,

$$\mathbf{a} = \mathbf{U}\mathbf{D}\mathbf{V}^{\dagger}\,. \tag{22}$$

Here $\mathbf{U}$ and $\mathbf{V}$ are unitary matrices and $\mathbf{D}$ denotes a diagonal matrix with diagonal elements d_j. Note that the decomposition (21) is always possible. $\mathbf{U}$ and $\mathbf{V}$ are the eigenvector matrices of $\mathbf{a}\mathbf{a}^{\dagger}$ and $\mathbf{a}^{\dagger}\mathbf{a}$, respectively. Next we introduce the sets of orthonormal functions $\{\hat{\phi}_i\}$ and $\{\hat{\chi}_i\}$ which are obtained by transforming the $\{\tilde{\phi}_i\}$ and $\{\tilde{\chi}_i\}$ with $\mathbf{U}^{\mathrm{T}}$ and $\mathbf{V}^{\dagger}$, respectively. The representation (19) expressed in these functions, which are just the natural functions introduced in section 2.2, assumes a diagonal form

$$\Psi(x,y,t) = \sum_{i=1}^{m} d_i(t)\,\hat{\phi}_i(x,t)\,\hat{\chi}_i(y,t)\,. \tag{23}$$

We recall that eqs. (19), (21) and (23) are all equivalent, i.e. they allow for the same approximation to the exact wave function. It is quite remarkable that the demand of orthogonality among *both* sets $\{\hat{\phi}_i\}$ and $\{\hat{\chi}_i\}$ does not reduce the trial space of the multi-configurational wave function Ψ. We emphasize that a transformation of the representation (1) (with $m_k = m$ for all k) to diagonal form (similar to the transformation (19)→(23)) is *not* possible for $n > 2$. In this case a diagonal ansatz (even with non-orthogonal functions) covers a smaller trial space than the ansatz (1).

The multi-configurational approaches of refs. [5,9] assumes an ansatz for the trial function Ψ which is identical to that in eq. (21) except that it requires orthogonality among the set $\{\tilde{\chi}_i\}$. It is clear from the discussion above that this ansatz covers the same trial

space as eqs. (19), (21) and (23). However, when propagating the wave functions, a set of fixed (time-independent) projectors is introduced to maintain the orthogonality among the set $\{\hat{\chi}_i\}$. This reduces the trial space for the propagated wave function and makes the propagated wave function $\Psi(t)$ to depend on the choice of the projectors. Our working equations conserve the orthogonality among the "single-particle" functions without the explicit introduction of projection operators. Because of the redundancy in our ansatz (1) we could require the orthogonality constraint (3) among the functions and their time derivatives. This constraint does not only conserve the orthogonality among the functions itself, it also considerably simplifies the working equations. Finally we emphasize again that our approach is generalized from the very beginning to treat any number of degrees of freedom as well as to contain any desired number of configurations.

3. Illustrative example

In this section we discuss a two-dimensional example as a first test of our approach to MCTDH. For two degrees of freedom the time-dependent Schrödinger equation can be solved (numerically) exactly providing the possibility for an unambiguous test. We consider the same model of coupled oscillators as in our previous investigation on TDRH [7]. The model is defined by the Hamiltonian

$$H=\tfrac{1}{2}(p_x^2+p_y^2+x^2+y^2)+\lambda(xy^2-\tfrac{1}{3}x^2) + \tfrac{1}{16}\lambda^2(x^2+y^2)^2, \qquad (24)$$

which may be recognized as a modified Hénon–Heiles potential [7,13]. We have chosen $\lambda=0.2$ and have assumed that the initial wave packet is a (separable) Gaussian centered at $x_0=1.8$, $y_0=0$ with momenta $p_{x0}=0$, $p_{y0}=1.2$ and width parameters $\langle(x-x_0)^2\rangle=0.56$, $\langle(y-y_0)^2\rangle=0.24$, having an energy $E=3.04$. In order to numerically solve the MCTDH working equations, all wave functions were expanded in a basis of harmonic oscillator functions. The differential equations (8) and (11) were solved by a predictor–corrector routine which uses variable step sizes.

The initial wave packet is a simple Hartree product: $\Psi(x,y)=\phi_1(x)\chi_1(y)$. Turning to MCTDH one has to specify the initial functions ϕ_j and χ_j for $j>1$. We have chosen $\phi_2\approx x\phi_1$, $\phi_3\approx x^2\phi_1$, etc., and have successively Schmidt orthogonalized these functions (and similar for the χ_j). For test purposes we have tried other much less reasonable initial "single-particle" functions. We have found that the propagated wave function $\Psi(t)$ is amazingly insensitive to the choice of the initial functions.

The initial coefficient matrix $\mathbf{a}=\left(\begin{smallmatrix}1&0\\0&0\end{smallmatrix}\right)$ is singular and a regularization is hence necessary. We have adopted the regularization eq. (18) and investigated the dependence of the computed wave function on ϵ. We found that for $10^{-16}\leqslant\epsilon\leqslant10^{-18}$ there are virtually no changes in the computed wave function. We have set $\epsilon=10^{-10}$ in the calculations reported below.

To gain information on the quality of the proposed MCTDH method, the overlaps between the TDH and MCTDH wave packets and the exact one have been calculated. The square moduli of these overlaps are shown in fig. 1. The results demonstrate a fast convergence of the MCTDH method as the number of configurations is increased. The error is approximately halved for each increment of m.

Fig. 2 shows the eigenvalues of $\mathbf{a}^\dagger\mathbf{a}$ as a function of time. The eigenvalues are the weights of the natural functions as discussed in section 2.2. For the special case $m=2$ treated here there is only one set

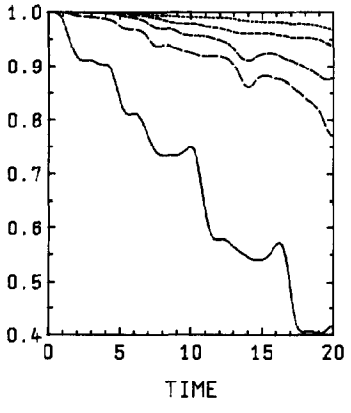

Fig. 1. Overlap square moduli as a function of time. The full line represents the overlap between the exact and the TDH wave functions. The dashed lines represent the overlaps between the exact and the MCTDH wave functions for $m=2$, 3, 4 and 5. The time $t=20$ corresponds to about three periods of the oscillator.

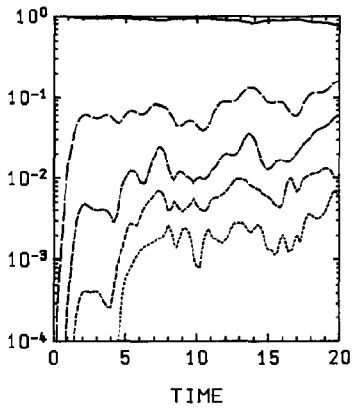

Fig. 2. The eigenvalues of $\mathbf{a}^{\dagger}\mathbf{a}$ as a function of time. Shown are the d_j^2 of the MCTDH calculation using five single-particle functions for each degree of freedom (i.e. $m=5$). The other calculations (i.e. $m=2$, 3 and 4) yield curves which are similar to the ones above, except that the lines for the smaller $d_j^2(t)$ functions are then missing.

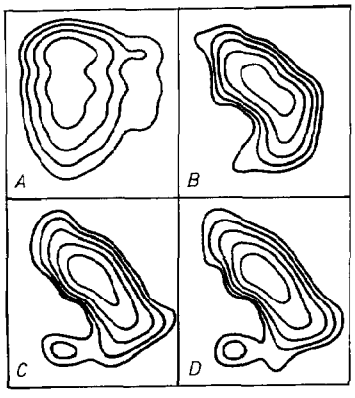

Fig. 3. Wave packet at time $t=20$. Shown are the equidensity lines of the modulus squared of the TDH wave packet (A), the MCTDH with $m=3$ (B) and $m=5$ (C) and the exact wave packet (D).

of weights (cf. eq. (20)). In order to be consistent with eqs. (22) and (23) we call these eigenvalues d_j^2. The results demonstrate that the weights of the natural functions in the wave packet drop rapidly (see fig. 2). The inspection of the weights is generally useful because they indicate whether a sufficient number of single-particle functions has been included in the calculation without the necessity to compare with an exact calculation (cf. section 2.2).

For illustrative purposes we finally show in fig. 3 plots of the equidensity lines of the wave packets propagated with one (TDH), three and five functions per degree of freedom (MCTDH) as well as the exact result. The plots are self-explanatory and need not to be commented.

4. Conclusions

We have presented a multi-configuration formalism to propagate a wave packet of several degrees of freedom. Our ansatz for the multi-configurational wave function is not unique; the same wave packet Ψ can be expressed by different coefficients and different "single-particle" functions. This redundancy, however, allows us to impose the constraint (3) when turning to the time evolution. The constraint (3) simplifies the resulting working equations considerably. These working equations are found to be well behaved numerically. An a priori choice of projection operators is not required.

We could define weights of the so-called natural functions. These weights, which are easy to compute, provide a very useful test on the convergence with respect to the number of functions included.

The MCTDH formalism presented here seems to be easily extendable to a multi-configuration time-dependent Hartree–Fock (MCTDHF) formalism for treating time-dependent problems of quantum chemistry or of nuclear physics.

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