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Lanczos-type algorithm for excited states of very-large-scale quantum systems

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We provide a very efficient procedure for obtaining the excited states of a quantum operator H, in any arbitrary chosen energy range, independently from the knowledge of the states at lower energies. Our procedure consists in determining, within the Lanczos algorithm, the ground state of the auxiliary operator $A=(H-E_t)^2$, and hence the eigenvalue of H nearest in energy to E_t, where E_t is any chosen trial energy in the energy range of interest. We show that a variational method exploiting diagonalization of 2×2 Lanczos matrices, combined with a two-pass Lanczos procedure of relatively small number of iterations, produces eigenvalues of H within any desired accuracy, as well as the corresponding eigenfunctions. We discuss in particular the $T\otimes\tau$ Jahn-Teller model, as a realistic prototype of a quantum system with a very large number of degrees of freedom.

I. INTRODUCTION

The theoretical investigation of numerous physical problems requires an appropriate handling of matrices of very large rank; among the many interesting physical problems, we can mention the Jahn-Teller vibronic systems,[1] extended or localized impurity states in semiconductors,[2] spin systems and Hubbard models,[3,4] and energy levels of solids, molecules, surfaces, and microstructures.[5-8] An accurate account of these systems may involve a large number of degrees of freedom; one often has to handle matrices of the order $N\approx 10^5$ or more, and therefore as many as 10^{10} matrix elements. Even if in many applications the matrix is sparse (that is the number of matrix elements different from zero as proportional to N rather to N^2), the problem cannot be solved by means of a direct diagonalization by standard routines.

The problem to treat large matrices and to extract the relevant physical quantities requires a joint and balanced technical and physical approach; for this reason, a vast array of techniques has been developed, with successful results in limited and specific situations.[9-12] In this framework, the Lanczos method and the related recursion method,[13-16] possibly with appropriate implementations, has emerged as one of the most important computational procedures, mainly when a few extreme eigenvalues (largest or smallest) are desired. Despite its well-documented merits, it is also well known that the Lanczos method may indeed present a number of difficulties, essentially connected to the loss of orthogonality among the states of the Lanczos chain due to finite-precision arithmetic.[17-19] This fact can produce the occurrence of spurious eigenvalues and ghost states. To avoid this problem, an orthogonalization to all states of the Lanczos hierarchy is required, but would be costly in terms of storage memory. In particular, if the interest is on the ground state of an operator H (or on its lowest-lying states), quite stable and accurate modified Lanczos-type approaches have been advanced in literature.[20,21]

In a previous paper,[22] we have presented some relevant aspects of a method for determining any desired excited state of a given operator; preliminary applications were, however, limited to one-dimensional systems[22] or to a test matrix[23] (the "modified Nesbet matrix"), and the method, although promising, needed further implementations to become a really workable tool. In this paper, in Sec. II, we present a relevant implementation of the Lanczos tridiagonalization scheme, which allows us to obtain a very fast convergence to any excited eigenvalue and eigenfunction of H, overcoming memory storage difficulties. As an exemplification of our procedure, in Sec. III, we consider in detail the $T\otimes\tau$ Jann-Teller system, and provide ground and excited eigenvalues, as well as eigenfunctions, for different coupling constants. Section IV contains the conclusions.

II. THE METHOD

The approach that we present allows us to determine the excited states in any desired energy range of any arbitrary operator, when its representation on a given basis set is known. No knowledge of the lower energy states is required. The present procedure enjoys the advantages of being variational, of fast convergence, and yet avoids the burden of further memory storage limitations. In practice, we can extend the Lanczos method, up to now used in literature essentially for the ground state of a system, to any excited state of those systems.

Let us consider an operator H, with unknown eigenvalues E_i and eigenfunctions $|\Psi_i\rangle$; any auxiliary operator $A=f(H)$ commutes with H, and thus shares with it a complete set of eigenfunctions corresponding to the eigenvalues $A_i=f(E_i)$. In order to obtain the excited state of H nearest in energy to any *a priori* chosen trial

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energy E_t, we consider the auxiliary operator A in the form $A=(H-E_t)^2$. Several other forms for A are possible; our choice of $f(H)$ in the specific quadratic power form is very easy and its application to any given state is straightforward. In a completely different context, this form is suggested by numerical analysis[24] to solve the Schrödinger equation within any desired energy. Recently it has been applied by Wang and Zunger[25] in the framework of the conjugate-gradient method. Thus, we are faced with the solution of the following eigenvalue equation:

$$A|\Psi_i\rangle \equiv (H-E_t)^2|\Psi_i\rangle = \lambda_i|\Psi_i\rangle \tag{1}$$

for the search of the ground state of A.

The strategy followed for the solution of Eq. (1) is essentially based on an appropriate implementation of the Lanczos algorithm. We briefly summarize some basic features of the Lanczos procedure in its standard formulation; we focus then on our implementation, which transforms the whole procedure into a workable and fastly convergent method.

Let us denote with $\{\varphi_i\}(i=1,2,\ldots,N)$ a complete set of basis functions, for the representation of the operator H (and hence of A). Starting from a seed state $|u_0\rangle$, given by whatever chosen linear combination of the $\{\varphi_i\}$, a hierarchical chain of orthonormal states $|u_0\rangle, |u_1\rangle, \ldots, |u_N\rangle$ is constructed via successive applications of the operator A as follows:

$$|U_1\rangle=(A-a_0)|u_0\rangle\ , \quad b_1^2=\langle U_1|U_1\rangle\ , \quad a_0=\langle u_0|A|u_0\rangle$$

and, in general,

$$|U_{n+1}\rangle = A|u_n\rangle - a_n|u_n\rangle - b_n|u_{n-1}\rangle\ ; \quad n>1\ . \tag{2}$$

The (non-normalized) state $|U_{n+1}\rangle$ allows us to determine the coefficients b_{n+1} and a_{n+1} of the $(n+1)$th iteration step, via the procedure

$$b_{n+1}^2 = \langle U_{n+1}|U_{n+1}\rangle\ , \tag{3a}$$

$$a_{n+1} = \frac{\langle U_{n+1}|A|U_{n+1}\rangle}{\langle U_{n+1}|U_{n+1}\rangle}\ . \tag{3b}$$

After normalization of the state $|u_{n+1}\rangle = |U_{n+1}\rangle / b_{n+1}$, the steps (2) and (3) are repeated with n replaced by $n+1$. The use of the operator $A=(H-E_t)^2$ instead of H of course poses no problem: in fact, it simply means to apply H, with E_t subtracted from its diagonal elements, to a given vector and repeat this same operation on the vector so obtained.

In the new basis $\{|u_n\rangle\}$ the operator A is represented by a tridiagonal Lanczos matrix T_m, whose elements $\{a_n\}$ and $\{b_n\}$ are explicitly known up to the order m $(m \le N)$ of the iterations performed. For what concerns how many iteration steps can be obtained in actual problems, there is a wide spread of situations depending on the physical problem at hand, on what is being calculated, whether the matrix elements are reasonable balanced or not, etc. Experience shows that, in general, it is hardly of any help to determine the tridiagonal matrix T_m for m higher than a few tens (say, hundred at most), due to the appearance of the Lanczos phenomena.[17,18] In fact the difficulty with the Lanczos method is that finite-precision arithmetic causes rounding errors, which manifest in loss of orthorgonality among the states $|u_n\rangle$; the remedy requires reorthogonalization and would be expensive in term of memory storage and time machine.

However if one is interested only to the ground state, as in treating with the operator A, the method suggested by the authors of Refs. 20 and 21 appears to be a good solution to this problem. Following this method, the iterative steps of the Eqs. (2) and (3) instead of being performed m times, are performed only once; hence the 2×2 Lanczos matrix is diagonalized and the eigenfunction $|g_0\rangle$ corresponding to the lowest eigenvalue α_0 of this secular problem, becomes the new initial state to repeat the cycle. Iteration of this "two-state relaxation" procedure generates a sequence of eigenvalues α_0, which approach variationally the desired eigenvalue $\lambda_0=(E_0-E_t)^2$.

It could seem, at first sight, that the problem is now solved; again our experience shows that this is not the case. In the first iterations α_0 decreases rapidly, but later much slower and finally the decreasing rate tends to vanish. The reason for this behavior is that, as the iteration number grows, the seed starting state, exploring all the physical manifold of states of the system spanned by the application of the operator A, approaches variationally the true ground state and, at the same time, has to decouple from all the other states of the chain; eventually, there is negligible improvement to insist in the 2×2 relaxation process. At this point, we override the two-state relaxation process and use the last obtained eigenfunction $|g_0\rangle$ as a starting state for a "two-pass" Lanczos procedure[16] of suitable order. For this, we construct a new Lanczos chain of m elements (m is of the order of few tens), hence we diagonalize the corresponding tridiagonal Lanczos matrix T_m obtaining its eigenvalues and the coefficients of the eigenvectors on the basis of the chain states $|u_n\rangle$. For our purposes, we select the lowest eigenvalue α_0 and the components $\{c_{n,0}\}$ of corresponding eigenfunction $|\Psi_0\rangle$:

$$|\Psi_0\rangle = \sum_{n=0}^{m} c_{n,0}|u_n\rangle\ .$$

Then because, for memory reason, in the three-term relation (2), we do not store all the vectors $|u_n\rangle$ when we determine T_m, we regenerate the states $|u_n\rangle$ with the same initial seed state $|g_0\rangle$ by a second Lanczos procedure. As far as storage requirements are concerned, we note that, with respect to the usual Lanczos procedure, we have to store only one further vector. An appropriate alternation of 2×2 relaxation processes and two-pass Lanczos procedures allows to obtain the ground state of A (and hence the excited state of H nearest to E_t) within the desired accuracy. In effect, is not possible to give a unique criterion for this alternation of 2×2 relaxation processes and two-pass Lanczos technique. The important fact is that the more efficient way to reach convergence is neither the 2×2 relaxation process nor the traditional Lanczos procedure. The problem is not a "principle" problem (mathematically the Lanczos method generates a perfectly orthonormal hierarchy of states); the problem is purely technical: one has to cope with the loss of orthogonality that unavoidably flaws the Lanczos procedure, due to finite-precision arithmetics. So only a general guideline can be given to treat situations that can be quite different, as we will discuss in the following section.

III. THE $T\otimes\tau$ JAHN-TELLER SYSTEM

In this section, we apply the method outlined so far to the $T\otimes\tau$ Jahn-Teller system, a well known[26] rather demanding example of vibronic system encountered in the framework of the dynamical Jahn-Teller effect in localized electron states.[1] As any other vibronic system, in the intermediate or strong coupling situation, it requires processing of a large number of electronic and vibrational states. These situations have been studied in the literature also by standard recursion techniques,[27,28] but extension to the strong coupling regimes can be done with the method illustrated in Sec. II.

The vibronic system under consideration is constituted by a threefold degenerate T_2 electronic state with T_d group symmetries, linearly coupled with a triply degenerate vibrational mode (τ_2 symmetry). In a cluster model,[29] by expanding the electron-phonon interaction energy up to the second order in the normal symmetrized coordinates Q_x, Q_y, Q_z, and taking into account the tetrahedral symmetry of the vibronic system, we obtain the following $T\otimes\tau$ Hamiltonian on the basis of the electronic wave function Ψ_x, Ψ_y, Ψ_z:

$$H=\frac{\hbar^2}{2M}\left[\frac{\partial^2}{\partial Q_x^2}+\frac{\partial^2}{\partial Q_y^2}+\frac{\partial^2}{\partial Q_z^2}\right]+V_\tau\begin{bmatrix}0 & Q_z & Q_y\\ Q_z & 0 & Q_x\\ Q_y & Q_x & 0\end{bmatrix}$$
$$+\tfrac{1}{2}M\omega^2(Q_x^2+Q_y^2+Q_z^2)\ . \tag{5}$$

In Eq. (5), the energy of the degenerate electronic state is taken as reference energy; V_τ is the linear coupling constant of the electronic state with the vibrational mode τ_2, and ω is the angular frequency of the mode; the quantities in Eq. (5) that are not written explicitly in matrix form are intended to be multiplied by the 3×3 identity matrix. This is a well-known Jahn-Teller Hamiltonian studied by a number of authors starting from the pioneer works of Ham,[30] Englman, Caner, and Toaff.[31]

It is convenient to adopt a second-quantization description introducing the phonon creation and annihilation operators a_x, a_x^+, a_y, a_y^+, a_z, and a_z^+ for the partner functions of the τ_2 mode; the corresponding states can be labeled by the integers l, m, n, respectively, which give their occupation numbers. The basis functions chosen are thus the direct product $|\Psi_i;lmn\rangle$ of the degenerate electronic functions $|\Psi_i\rangle (i=x,y,z)$ and the vibrational states $|lmn\rangle$. On the basis functions $|\Psi_i;lmn\rangle$, the Hamiltonian (5) can be written as

$$H=H_L+H_{e-L}\ , \tag{6a}$$

where the lattice Hamiltonian is

$$H_L=\sum_{\substack{i=x,y,z\\ l,m,n=0,\infty}}(l+m+n+\tfrac{3}{2})\hbar\omega|\Psi_i;lmn\rangle\langle\Psi_i;lmn|\ , \tag{6b}$$

and the electron-lattice interaction H_{e-L} is

$$H_{e-L}=k_\tau\sum_{l,m,n}[|\Psi_x;lmn\rangle\langle\Psi_y;lmn|$$
$$+|\Psi_y;lmn\rangle\langle\Psi_x;lmn|](a_z+a_z^+)+\cdots\ , \tag{6c}$$

where the dots summarize cyclic interchange of x,y,z indices. The adimensional coupling constant k_τ is equal to $2V_\tau/[\sqrt{3}(2M\hbar)^{1/2}\omega^{3/2}]$ and is related to the Huang-Rhys factor S by the standard relation $S=\frac{2}{3}k_\tau^2$.

Following the method described in Sec. II, we can obtain the eigenvalues and the eigenfunctions of the Hamiltonian (5) for any excited state and for any strength of the coupling constant k_τ. We discuss below some aspects of the solution, whose relevance is beyond this specific problem.

First the 2×2 relaxation procedure is performed with the operator A. We soon confirm that the converge rate is the lowest eigenvalue α_0 is very fast for the initial iterations, but then it decreases and eventually tends to vanish. In effect it is easy to verify that the eigenvalue correction is of the order of $|b_1|^2/(\alpha_0-\alpha_1)$, α_0, α_1, b_1 being the diagonal and off-diagonal elements of the 2×2 Lanczos chain, and this correction becomes extremely small as the off-diagonal element b_1 decreases. In our case, when the monotonic decreasing of b_1 stops, we start the two-pass Lanczos procedure. We have chosen to handle relatively small tridiagonal matrices (of the order of 50 at maximum), and then to repeat, whenever necessary, a number of two-step relaxations and two-pass Lanczos processes. The global procedure stops when the first recursion coefficient b_1 becomes smaller than a chosen precision coefficient ε.

At convergence, the mean value $E_0=\langle\Psi_0|H|\Psi_0\rangle$, and one of the roots $E_0^*=E_t\pm\sqrt{\alpha_0}$ must be coincident. In our case, with ε of the order of 10^{-5} we can obtain E_0 and E_0^* coincident at least until eight significative figures. In Fig. 1 we show, for a given excited state, the behavior of the lowest eigenvalue α_0 of A with a 2×2 relaxation processes, alternated with one two-pass Lanczos procedure of order 20 and 50. The convenience of the introduction of the two-pass Lanczos procedure is evident.

We wish to notice that the overall number of iterations and states involved for the convergence, depends on the strength of the Jahn-Teller coupling or, in other terms, on the value of S: large values of S involve large number of phonons and of basis functions. For instance, for $k_\tau=3$, eigenvalues accurate up to 9 significant figures require 17 phonons in each direction and hence $N=3\times18^3=17\,496$ basis functions.

In Fig. 2 we show the vibronic energy levels corresponding to the different representations of the group T_d, as functions of the coupling constant k_τ; these energy values are in agreement, with previous calculations,[27,31] usually available only for small k_τ.

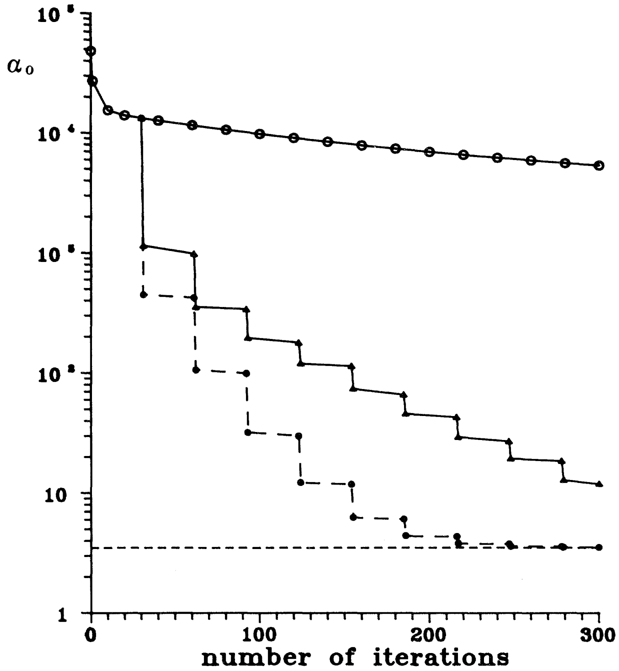

FIG. 1. Behavior of the lowest eigenvalue α_0 of the matrix A (corresponding to the 5th excited state of T_2 symmetry and $k_\tau=2$) vs the number of iterations. (-○-) Two-step relaxation process; (-▲-) two-step relaxation process alternated with one two-pass Lanczos procedure of order 20; (-●-) two-step relaxation process alternated with one two-pass Lanczos procedure of order 50. The horizontal dashed line indicates the asymptotic value λ_0. Energies are in units of $10^{-4}\hbar\omega$.

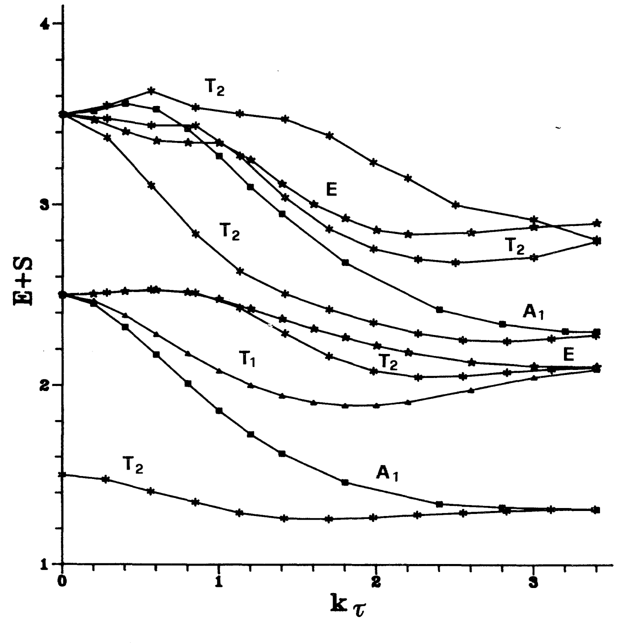

FIG. 2. Vibronic energy levels for $T\otimes\tau$ Jahn-Teller vs the coupling constant k_τ. The levels are labeled according to the irreducible representations of the group T_d; $\hbar\omega$ is the unit of energy.

Our technique allows also to obtain the eigenfunctions for any state; thus, we can calculate, as a significant test, some "effective factors" for the ground state. They are well known in literature as the "reduction factors" $K(E)$, $K(T_2)$, and $K(T_1)$, first introduced by Ham,[30] and defined, in general, as follows:

$$K(E)=\frac{\langle \Phi_z^{T_2}|E_\theta|\Phi_z^{T_2}\rangle}{\langle \Phi_z^{T_2}|E_\theta|\Phi_z^{T_2}\rangle_{k_\tau=0}}\ , \tag{7a}$$

$$K(T_2)=\frac{\langle \Phi_x^{T_2}|T_z|\Phi_y^{T_2}\rangle}{\langle \Phi_x^{T_2}|T_z|\Phi_y^{T_2}\rangle_{k_\tau=0}}\ , \tag{7b}$$

$$K(T_1)=\frac{\langle \Phi_x^{T_2}|L_z|\Phi_y^{T_2}\rangle}{\langle \Phi_x^{T_2}|L_z|\Phi_y^{T_2}\rangle_{k_\tau=0}}\ , \tag{7c}$$

where $\Phi_x^{T_2}$ $(\Phi_y^{T_2},\Phi_z^{T_2})$ is the vibronic eigenfunction of the total electron-phonon Hamiltonian transforming as the x (y,z) row of the T_2 irreducible representation of the T_d group. Here the electronic operators E_θ, L_z, and T_z are represented, on the degenerate electronic triplet, by the following matrices:

$$E_\theta=\begin{bmatrix}\frac{1}{2} & 0 & 0\\ 0 & \frac{1}{2} & 0\\ 0 & 0 & -1\end{bmatrix}$$

$$=\tfrac{1}{2}(|\Psi_x\rangle\langle\Psi_x|+|\Psi_y\rangle\langle\Psi_y|)-|\Psi_z\rangle\langle\Psi_z|\ , \tag{8a}$$

$$T_z=\begin{bmatrix}0 & -1 & 0\\ -1 & 0 & 0\\ 0 & 0 & 0\end{bmatrix}=-(|\Psi_x\rangle\langle\Psi_y|+|\Psi_y\rangle\langle\Psi_x|)\ , \tag{8b}$$

$$L_z=\begin{bmatrix}0 & -i & 0\\ i & 0 & 0\\ 0 & 0 & 0\end{bmatrix}=-i(|\Psi_x\rangle\langle\Psi_y|-|\Psi_y\rangle\langle\Psi_x|)\ . \tag{8c}$$

In our notation, we can write the vibronic function transforming as the z row of the T_2 irreducible representation as

$$\Phi_z^{T_2}=\sum_{l,m,n} c_{x,lmn}^{(z)}|\Psi_x;lmn\rangle$$
$$+c_{y,lmn}^{(z)}|\Psi_y;lmn\rangle+c_{z,lmn}^{(z)}|\Psi_z;lmn\rangle\ . \tag{9}$$

Taking into account the Eqs. (7a) and (8) we obtain

$$K(E)=-\frac{1}{2}\left[1-3\sum_{lmn}|c_{z,lmn}^{(z)}|^2\right]\ . \tag{10}$$

As a consequence of the symmetry of the problem, we have

$$\sum_{lmn}|c_{z,lmn}^{(z)}|^2=1-2\sum_{lmn}|c_{z,lmn}^{(x)}|^2\ .$$

We can thus express

$$K(E)=1-3\sum_{lmn}|c_{z,lmn}^{(x)}|^2\ , \tag{11a}$$

in terms of the z component of the vibronic function

TABLE I. Effective factors $K(T_2)$, $K(T_1)$, and $K(E)$ for the ground vibronic state. N is the number of basis functions included. In the brackets we report the values calculated by O'Brien.[32]

k_τ	N	$K(T_2)$	$K(T_1)$	$K(E)$
0.5	1 029	0.902 09	0.715 99	0.720 85
		(0.902 09)	(0.716 00)	(0.720 85)
1.	3 000	0.760 77	0.339 74	0.368 42
		(0.760 97)	(0.339 77)	(0.368 17)
1.5	8 232	0.678 67	0.130 40	0.176 95
		(0.678 67)	(0.130 40)	(0.176 95)
2.	10 125	0.650 20	0.037 97	0.077 13
		(0.652 0)	(0.037 97)	(0.077 13)
2.5	12 288	0.649 15	0.007 29	0.024 30
		(0.649 2)	(0.007 29)	(0.014 48)
3.	17 496	0.653 25	0.912×10^{-3}	0.004 79
		(0.653 2)	(0.000 1)	(0.004 8)
4.	31 944	0.659 40	0.50×10^{-5}	0.526×10^{-4}
5.	98 304	0.662 24	$<10^{-8}$	0.12×10^{-6}
6.	128 625	0.663 67	$<10^{-11}$	$<10^{-10}$

transforming as the x row of the T_2 irreducible representation.

The effective factors $K(T_2)$ and $K(T_1)$ also, can be given in terms of the components of the same vibronic function in this way:

$$K(T_2)=\sum_{lmn}(c_{x,lmn}^{(x)}c_{x,mln}^{(x)}+c_{y,lmn}^{(x)}c_{y,mln}^{(x)})\ , \tag{11b}$$

$$K(T_1)=\sum_{lmn}(c_{x,lmn}^{(x)}c_{x,mln}^{(x)}-c_{y,lmn}^{(x)}c_{y,mln}^{(x)})\ . \tag{11c}$$

These first-order reduction factors are compared with previous calculations of O'Brien,[32] as shown in Table I, where the values calculated by means of our procedure have accuracy within nine significant figures, and hence we consider this calculation a very significant test of the technique proposed.

In principle it would be possible to calculate, in a similar way, also second-order reduction factors, because they involve matrix elements of a perturbation operator between ground and excited states. However, this would require a lot of work, certainly important in a perturbative approach, as discussed in many significant papers.[32–35] We notice, however, that our procedure is not perturbative, it is very flexible, and allows us to consider exactly, on the same footing both the Jahn-Teller interaction as other interactions of physical interest (for instance spin-orbit interaction, magnetic or electric field, uniaxial stress, etc., regardless of the relative importance of the various contributions) treating with the same method the total Hamiltonian of the system. Perturbative approaches can thus be avoided, and the limit of the procedure is not the Hamiltonian but the number of basis functions that can be handled. These considerations should be of value, in particular, in those Jahn-Teller or pseudo Jahn-Teller systems (impurities in II-VI or III-V compounds, *F* centers) subjected also to an external perturbation, where a diagonalization made within the traditional Lanczos scheme[28] has given good results, only for the ground or lowest lying energy states.

IV. CONCLUSIONS

We have presented a very efficient method to evaluate the excited states of a quantum system with a large number of degrees of freedom. The advantages of our method ar numerous, in particular explicit determination of the lower energy states and orthogonalization to them is unnecessary, the convergence is satisfactory, and memory storage difficulties are avoided. As an examplification of the procedure, we have examined the $T\otimes\tau$ Jahn-Teller system. The results obtained provide confidence that our method should become a very precious one in all the numerous problems of physics, where a large basis set is needed.

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[1] *The Dynamical Jahn-Teller Effect in Localized Systems,* edited by Yu. E. Perlin and M. Wagner (North-Holland, Amsterdam, 1984).

[2] See, for instance, R. D. Graft, G. Grosso, D. J. Lohrmann, L. Martinelli, S. Moroni, G. Pastori Parravicini, and L. Resca, in *Progress in Electron Properties of Solids,* edited by E. Doni, R. Girlanda, G. Pastori Parravicini, and A. Quattropani (Kluwer, Dordrecht, 1989), p. 409.

[3] See, for instance, K. W. Stevens, Physica B **176**, 1 (1992).

[4] E. Dagotto and J. R. Schrieffer, Phys. Rev. B **43**, 8705 (1991); H. J. Cannon, R. T. Scalettar, and E. Fradkin, *ibid.* **44**, 5995 (1991); H. J. Schulz and T. A. L. Ziman, Europhysics Lett. **18**, 355 (1992); J. Song and J. F. Annett, *ibid.* **18**, 549 (1992).

[5] M. P. Payne, M. P. Teter, D. C. Allan, T. A. Arias, and J. D. Joannopoulos, Rev. Mod. Phys. **64**, 1045 (1992).

[6] J. L. Martins and M. L. Cohen, Phys. Rev. B **37**, 6134 (1988); J. L. Martins, N.Troullier, and S. H. Wei, *ibid.* **43**, 2213 (1991).

[7] G. Grosso, S. Moroni, and G. Pastori Parravicini, Phys. Rev. B **40**, 12 328 (1989).

[8] L. W. Wang and A. Zunger, J. Phys. Chem. **98**, 2158 (1994).

[9] See, for instance, D. R. Pooler, in *The Dynamical Jahn-Teller Effect in Localized Systems,* edited by Yu. E. Perlin and M. Wagner (North-Holland, Amsterdam, 1984).

[10] E. R. Davidson, Comput. Phys. **7**, 519 (1993), and references quoted therein.

[11] D. M. Wood and A. Zunger, J. Phys. A **18**, 1343 (1985).

[12] T. Koslowski and W. von Niessen, J. Comp. Chem. **14**, 769 (1993).

[13] C. Lanczos, J. Res. Natl. Bur. Stand. **45**, 255 (1950); **49**, 33 (1952); *Applied Analysis* (Prentice-Hall, Englewood Cliffs, NJ, 1956).

[14] R. Haydock, V. Heine, and M. J. Kelly, J. Phys. C **5**, 2845

(1972); **8**, 2591 (1975); see also D. W. Bullet, R. Haydock, V. Heine, and M. J. Kelly, in *Solid State Physics: Advances in Research and Applications*, edited by H. Erhenreich, F. Seitz, and D. Turnbull (Academic, New York, 1980), Vol. 35.

[15] G. Grosso and G. Pastori Parravicini, Adv. Chem. Phys. **62**, 81 133 (1985), and references quoted therein. See also P. Giannozzi, G. Grosso, S. Moroni, and G. Pastori Parravicini, Appl. Num. Math. **4**, 273 (1988).

[16] H. Q. Lin and J. E. Gubernatis, Comput. Phys. **7**, 400 (1993).

[17] L. W. Wang and A. Zunger, Comp. Mat. Sci. **2** (2) (1994).

[18] J. C. Cullum and R. A. Willoughby, in *Lanczos Algorithms for Large Symmetric Eigenvalue Computations* (Birkhauser, Boston, 1985), Vols. I and II.

[19] B. N. Parlett, *The Symmetric Eigenvalue Problem* (Prentice-Hall, Englewood Cliffs, NJ, 1980).

[20] J. Alberty, J. Greensite, and A. Patkos, Phys. Lett. B **138**, 405 (1984); E. Dagotto and A. Moreo, Phys. Rev. D **31**, 865 (1985).

[21] E. R. Gagliano, E. Dagotto, A. Moreo, and F. C. Alcaraz, Phys. Rev. D **34**, 1677 (1986); E. R. Gagliano and C. A. Balseiro, Phys. Rev. Lett. **59**, 2999 (1987); E. R. Gagliano and S. Bacci, Phys. Rev. D **36**, 546 (1987).

[22] G. Grosso, L. Martinelli, and G. Pastori Parravicini, Nuovo Cimento D **15**, 269 (1993).

[23] A. Cordelli, G. Grosso, and G. Pastori Parravicini, Comput. Phys. Commun. **83**, 255 (1994).

[24] J. C. Nash, *Compact Numerical Methods for Computers* (Hilger, Bristol, 1979).

[25] Lin-Wang Wang and Alex Zunger, J. Chem. Phys. **100**, 2394 (1994).

[26] R. Englman, *The Jahn-Teller Effect in Molecules and Crystals* (Wiley, New York, 1972).

[27] N. Sakamoto and S. Muramatsu, Phys. Rev. B **17**, 868 (1978); J. Phys. Soc. Jpn. **46**, 1273 (1979); M. C. M. O'Brien and S. N. Evangelou, J. Phys. C **13**, 611 (1980); M. C. M. O'Brien, *ibid.* **16**, 85 (1983); **16**, 6345 (1983); **18**, 4963 (1985).

[28] L. Martinelli, M. Passaro, and G. Pastori Parravicini, Phys. Rev. B **39**, 13 343 (1989); **43**, 8395 (1991); L. Martinelli and G. Pastori Parravicini, *ibid.* **46**, 15 795 (1992).

[29] M. D. Sturge, in *Solid State Physics: Advances in Research and Applications*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1967), Vol. 20, p. 92.

[30] F. S. Ham, Phys. Rev. **138**, A1727 (1965).

[31] M. Caner and R. Englman, J. Chem. Phys. **44**, 4054 (1966); R. Englman, M. Caner, and S. Toaff, J. Phys. Soc. Jpn. **29**, 306 (1970).

[32] M. C. M. O'Brien, J. Phys. Condens. Matter **2**, 5539 (1990).

[33] C. A. Bates and L. Dunn, J. Phys. Condens. Matter **1**, 2605 (1989); J. L. Dunn, C. A. Bates, and P. J. Kirk, *ibid.* **2**, 10 379 (1990).

[34] Y. M. Liu, J. L. Dunn, and C. A. Bates, J. Phys. Condens. Matter **6**, 859 (1994); **6**, 7521 (1994).

[35] V. Z. Polinger, C. A. Bates, and J. L. Dunn, J. Phys. Condens. Matter **3**, 513 (1991); V. Z. Polinger, P. J. Kirk, J. L. Dunn, and C. A. Bates, *ibid.* **5**, 2213 (1993).