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Multi-reference-state perturbation theory for computation of potential-energy surfaces*

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The implementation of multi-reference-state Rayleigh-Schrödinger perturbation theory for the evaluation of potential-energy surfaces is reviewed. The organization of the computation and the basic algorithms are outlined. A major difficulty is the quadratic increase in computing sources as the reference space is expanded. Truncating the space of nonreference determinants is suggested as a solution for the problem. The method applies a numerical cutoff criterion for the weights of the first-order wave function. The truncation reduces the computing time significantly with negligible sacrifice in the quality of the results.

Key words: Multireference perturbation theory — Potential-energy surface calculations

1. Introduction

A reliable method for computing accurate potential-energy surfaces (PES) of molecules, should in principle be able to track the variations in both configuration mixing and the electronic correlation energy as a function of the molecular geometry. Basically, all methods of electronic structure theory provide a set of systematic approximations to the exact solution. A practical PES method should reach the desired accuracy at rather low level of approximation without destroying the overall shape; that is, giving comparable accuracies at different geometries.

Perturbation-theory methods, e.g. the Rayleigh-Schrödinger (RS) series [1, 2] or coupled-cluster expansions [3, 4], are due to the linked-cluster theorem

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** *Present address:* IFF der Kernforschungsanlage, D-5170 Jülich, Federal Republic of Germany conceptually suitable for the purpose of computing PES. The linked-cluster theorem ensures that in every order, the terms entering the final perturbation expansion are all legal contributions appearing also in the infinite-order energy expression. In other words, even if topologically spurious terms are hidden in the perturbative formulae, they all mutually cancel at every order of the perturbation. The order-by-order perturbation results form therefore successive approximations to the energy.

By way of contrast, the importance of accumulating just the legitimate terms of the final energy expresion, is emphasized in variational methods like configuration interaction (CI) [5]. Here every approximation amounts to a partial infinite-order summation of the perturbation expansion, and as such it may include also spurious terms. For example, a CI expansion spanning only the single and double excitations out from some reference determinant (SDCI), gives an energy expression containing terms that cancel out when triples and quadruples are introduced [6, 7]. This accumulation of spurious terms is commonly referred to as the size-consistency error. It poses a serious problem for PES evaluation because the magnitude of spurious terms usually varies with the spatial configuration of the nuclei. To offset for this error the SDCI result is corrected by a perturbative estimate for the contribution of the illegal (unlinked) terms; the so called Davidson correction [6].

All stationary perturbation theories may be formulated beginning from a partitioning of Hilbert space into a small set of reference functions of interest (the reference space) and its orthogonal complement [8]. An effective Hamiltonian (H_{eff}) is then defined over the reference space under the requirement that its spectrum intersects with that of the original Hamiltonian. The elements of the matrix of H_{eff} are expandable as power series in the perturbation which is the difference operator between the exact and the zeroth-order Hamiltonian defining the basis. An order-by-order truncation of the perturbation series for H_{eff} gives a sequence of model effective Hamiltonians whose spectra constitute (if convergent) a set of systematic approximations to some eigenvalues of the exact Hamiltonian.

In the usual formulation of perturbation theory the reference space is never specifically defined. In fact, it is a free parameter of the theory; presumably the only one. It is clear that if the reference space poorly describes states of the perturbed Hamiltonian, then the perturbation expansion is for certain divergent [2, 9]. For example, think of a near-degeneracy situation of two configurations with just one of them defined as the reference space. By the same token, it is conceivable that varying the reference space (i.e. expanding it) may significantly improve the convergence of the perturbation expansion [9]. This improvement is directly related to the ability of the reference space to describe the wave functions in question. A quantitative measure of such a description is the weight of the reference space in the wave functions. The larger the weight, the better the convergence should be. Expanding the reference space will always increase the weight. Hence, this is a method of obtaining systematic approximations to the energy, in addition to the order-by-order truncation of the series.

The reference space is a degree of freedom of perturbaton theory which is necessary for PES calculations because of configuration mixing. It is the rule rather than the exception, that over a wide range of molecular geometries, the electronic wave function consists of a number of major configurations. This may be due to near-degeneracy effects as in forbidden curve crossing, or to improper description of dissociation by the zeroth-order functions, or simply to the influence of strong electronic correlations. A multi-reference-state (MRS) perturbation formalism which allows for configuration mixing and is also naturally size consistent, is therefore particularly suitable for the calculation of PES.

An extended reference space may prove quite costly in computing sources which increase quadratically with the number of reference states. It is crucial therefore that efficient computational procedures are employed. In this article we shall discuss how to organize an MRS perturbation calculation to third order. Means to increase efficiency are suggested. One is parallel processing which may be easily incorporated in the perturbation calculation. Another is trimming the orthogonal complement of the reference space. This method is frequently employed in MRS SDCI [10]. Here the discarded configurations are those which are unimportant (according to a numerical criterion for the weight) in the first-order RS wave function. This truncation has no significant effect on the third-order result but largely diminishes the computer sources needed. Trial calculations on Li_2 support this statement.

2. The multi-reference-state perturbation calculation

Let H^0 be the mean-field (e.g. Hartree–Fock) model Hamiltonian for a molecular system with the electronic Hamiltonian H at a specified geometry. The eigenvectors of H^0 are Slater determinants constructed from orbitals satisfying the mean-field equations. The zeroth-order energy associated with each determinant is a sum of its orbital energies. All these quantities are assumed known, and so is the matrix of the perturbation $V = H - H^0$ in the basis of Slater determinants. An element in this matrix is a linear combination of two-electron integrals between orbitals.

A small set p of determinants is chosen as the reference space. P is the projection operator onto the reference space and $Q = 1 - P$ projects onto q, the orthogonal complement of p. The determinants spanning the q-space are calssified as interacting or noninteracting with the reference space. The former group includes all the q-determinants that have a nonvanishing perturbation matrix element with at least one reference determinant. The set of interacting q-determinants is a subset of the union of single and double excitations from all p-determinants. The noninteracting q-determinants are: (i) Single and double excitations that due to symmetry have vanishing matrix elements with all the p-determinants. (ii) Triple and higher excitations with respect to any reference determinant. A perturbation calculation to third order involves only the interacting q-determinants. The entire Hamiltonian matrix is therefore the same as in MRS SDCI. Here however, it remains undiagonalized and is only used to construct the smaller matrices of the approximate RS effective Hamiltonians. This construction is the heart of the perturbation calculation as the diagonalization of the effective Hamiltonians is a simple matter. Note that by avoiding the diagonalization of the full SDCI matrix the size-consistency error is eliminated [6, 7].

To third order in V the RS effective Hamiltonians H^n_{RS} are [9]

$$H^1_{\mathrm{RS}} = PHP = PH^0P + PVP, \tag{1}$$

$$H^2_{\mathrm{RS}} = PHP + PVG^0_0VP, \tag{2}$$

$$H^3_{\mathrm{RS}} = PHP + PVG^0_0VP + PVG^0_0VG^0_0VP - PV[G^0_0]^2VP(H - E^0)P, \tag{3}$$

where

$$G^0_0 = [E^0 - H^0]^{-1}Q, \tag{4}$$

and E^0 (the reference energy) is the zeroth-order energy of the reference determinant that energy-wise is the most isolated from q-space.

To compute H^3_{RS} three $\dim(p)\times\dim(p)$ hermitian matrices are required: PVG^0_0VP, $PVG^0_0VG^0_0VP$ and $PV[G^0_0]^2VP$. The calculation of these matrices may be organized by columns where taking advantage of hermiticity, one element is to be computed from the first, two from the second, etc. Exploiting molecular symmetry a further reduction of computations is achieved, as only symmetry-wise unique elements are needed to construct the effective Hamiltonians. In any case, the number of elements to be computed scales quadratically with the size of the reference space. Because the nature of the PES problem dictates using extended reference spaces, the computation may quickly run out of hands. An important asset of the method is that it allows other means of reducing computing sources on a physical basis. Namely, the truncation of q-space [10].

The initial step is to obtain the nonzero elements of the rectangular matrix PVQ in full. They are stored by rows along with labels identifying the excitation from the p-determinant of the row. Given the orbitals occupied in the p-determinant, an excitation label uniquely defines a q-determinant. Even with large basis sets, the construction of the PVQ matrix is relatively fast and easy. Thus, this step can be repeated with each column if storage capacity is low.

The hard and time-consuming task is computing the columns of the third-order matrix $PVG^0_0VG^0_0VP$; it is equivalent to building an MRS SDCI matrix. The columns of the second-order matrices PVG^0_0VP and $PV[G^0_0]^2VP$ can be computed jointly with the identical columns of the third-order matrix. All the information needed to compute a second-order matrix element is also required in the computation of the same element in third order. A joint calculation can therefore be performed at negligible increase in time and with no additional storage requirements. Note that because the calculation is organized by columns, and since each column is computed independently, it is also possible to process columns in parallel. This could be arranged within the same run if a parallel processor is available, or alternatively in separate runs.

Consider therefore the column α for which the diagonal and $\alpha - 1$ elements are to be computed. The first stage is to construct the row α of the second-order rectangular matrix PVG^0_0VQ. Actually, for the third-order elements only a part of the row is needed. This part is the set of nonvanishing second-order interactions between the p-determinant Φ_α and all the single and double excitations out of it. Basically, the q-subspace here is the same as the one corresponding to the nonvanishing elements of the row α in the first-order matrix PVQ. There are some additional q-determinants though, which due to symmetry have a vanishing interaction with Φ_α in the first order, but not in the second. The formula for the second-order interaction of Φ_α with a q-determinant Φ_j is

$$\langle\Phi_\alpha|VG_0^0V|\Phi_j\rangle = \sum_{i\in q} \langle\Phi_\alpha|V|\Phi_i\rangle[E^0 - E_i]^{-1}\langle\Phi_i|V|\Phi_j\rangle, \tag{5}$$

where E_i is the zeroth-order energy of Φ_i. In practice, the summation in the equation above runs only over the set of single and double excitations out of Φ_α having a nonzero perturbation matrix element with it. This computed set of second-order interactions should be stored along with excitation labels identifying the q-determinants. The computation described here is clearly very similar to building an SDCI matrix and thus can be performed efficiently using unitary-group [11–13], or other algorithms [14, 15] for the construction of long configuration expansions. Our approach is based on diagrammatic many-body techniques [2].

Basically, there are three tasks in the calculation: (i) Creating a list of (i.e. identifying) the nonvanishing QVQ matrix elements according to the excitation labels of the row α in the PVQ and PVG_0^0VQ matrices. (ii) Sorting the two-electron integrals and computing the nonzero QVQ matrix elements. (iii) Computing the second order interactions according to (5). Proceeding straightforward in this order is not recommended on grounds of efficiency. The reason is that part (ii) is rather time consuming to perform. Also the list of nonvanishing QVQ elements is generally huge. For example, in a calculation performed on the ground-state determinant of Li_2 with 9863 single and double excitations, ~4.6 million nonzero elements were obtained in the lower triangular half of QVQ. Evidently it means that by calculating the list (i) first, one must scan the two-electron integrals many times because of storage limitations. A more sensible way to go is to unite steps (i) to (iii). That is, scanning once the two-electron integrals and adding them directly to the proper elements of the second-order row according to formula (5). This procedure requires identifying the QVQ matrix elements to which every two-electron integral contributes to (in many cases more than one). Only elements between the q-determinants in row α of PVQ and PVG_0^0VQ appear in (5). We employ diagrammatic-like techniques [2] to subdivide the sort of the labels of row α which identifies the QVQ elements. It is this part of the computation of diagonal elements that a truncation of q-space is most helpful for, since it reduces the number of elements in the row α. Lastly, we mention that although the present algorithm seems efficiently organized, it is not unlikely that on applying the unitary group method [11–13], or other techniques of wave function construction [14, 15] a faster computation of diagonal elements will result.

After row α of the second-order interaction matrix is obtained, the computation of the third-order diagonal element is as trivial as the second-order one. The corresponding formula is

$$\langle\Phi_\alpha|VG_0^0VG_0^0V|\Phi_\alpha\rangle=\sum_{i\in q}\langle\Phi_\alpha|V|\Phi_i\rangle[E^0-E_i]^{-1}\langle\Phi_i|VG_0^0V|\Phi_\alpha\rangle. \tag{6}$$

A simultaneous computation of the second- and third-order elements is carried out as follows: Each element in row α of PVQ is first divided by its corresponding energy-difference denominator (see (6)). Then a scalar product of the resulting array with the row α of PVQ and PVG_0^0VQ is performed to give, respectively, the diagonal second- and third-order elements. The array containing the elements of the row α of PVQ divided by their energy denominators, should be stored for subsequent computations of the $\alpha-1$ off-diagonal elements of column α. This phase of the calculation is discussed below.

The set of single and double excitations from the p-determinant Φ_β $(\alpha\neq\beta)$ is in general different from that of Φ_α. This means that it includes triples, quadruples, and possibly higher excitations with respect to the latter. The first step is therefore to classify the singles and doubles appearing in the list for p-determinant Φ_β according to their excitation level with respect to Φ_α. Excitations higher than quadruple are discarded as they cannot participate in the expansion below fourth order. Those excitations classified as singles and doubles contribute to the off-diagonal elements already in second order. Their contribution in second and third order, equals the scalar product of the first-order interactions (divided by energy denominators) of Φ_β with the first- and second-order interactions of the p-determinant Φ_α, respectively.

The second-order interactions connecting Φ_α to a triple excitation from it are topologically divided into linked and unlinked. The quadruples are connected to Φ_α only via unlinked interactions. To compute a second-order unlinked interaction is relatively simple, since any such interaction consists of a product of two matrix elements from the row α of PVQ divided by an energy denominator. Some superfluous (exclusion-principle-violating [1, 2]) terms enter the expansion through products leading to triple excitations. They cancel out however, by similar superfluous terms coming from the linked interactions [2]. Obtaining the linked triple-excitation terms is the difficult phase in the calculation of the off-diagonal elements. The procedure is simlar to that employed for computing the diagonal third-order terms. The two-electron integrals are scanned one by one, and a diagrammatic algorithm (the same as in the diagonal case) determines those which connect, in a linked fashion, a (triple) element in the row β of the PVQ matrix with an element in the row α. Every time such a linked interaction is spotted it is multiplied by the corresponding product of PVQ elements from rows α and β divided by the proper energy terms, and the result is added to $\langle\Phi_\beta|VG_0^0VG_0^0V|\Phi_\alpha\rangle$.

The entire calculation of the linked triple terms in an off-diagonal element is roughly between 25% to 40% of the calculation time for a third-order diagonal element. This estimation is based on the fraction (obtained in trial calculations) of elements in one row of PVQ, which correspond to triple excitations with respect to the p-determinant of another row. This effort in itself would not seem too demanding, except that in an MRS perturbation calculation one anticipates many off-diagonal elements. Moreover, as their number increases quadratically with the dimensionality of the reference space, computing the off-diagonal elements is expected to become the major task when expanded reference spaces are employed.

At this point it seems appropriate to invoke parallel processing; preferably in the same run. Because the computation of all the off-diagonal terms other than the linked triple excitations is relatively easy, they can be processed sequentially element by element. From each element the labels and the *PVQ* elements of triple excitations with respect to the *p*-determinant labelling the column (i.e. Φ_α) are stored in the computer core. After the allotted storage is exhausted we then proceed to compute the linked triple terms contributing to different off-diagonal elements in parallel. Batches of two-electron integrals are loaded into core one by one. Each batch is then processed in parallel for all the off-diagonal elements now stored in core memory. The procedure for each element was described in the previous paragraph. This is repeated until all two-electron integrals have been scanned. This type of parallel processing would greatly reduce the overall CPU and real times of the off-diagonal phase of the computation. Actually the present code is organized precisely as described above, except that instead of parallel processing, the stored off-diagonal elements are treated sequentially. Thus, parallel computations can be performed with just minor modifications.

Once the matrices PVG_0^0VP, $PVG_0^0VG_0^0VP$ and $PV[G_0^0]^2VP$ are obtained, it is straightforward to compute H_{RS}^2 and H_{RS}^3 using formulae (2) and (3). Observe that H_{RS}^3 is inherently nonhermitian even though it is constructed solely from hermitian matrices. This is because the product matrix $PV[G_0^0]^2VP(H-E^0)P$ will not be symmetric when the reference space is not exactly degenerate. Only when it is, will H_{RS}^3 be an hermitian matrix.

We wish to remark that although diagrammatic notions are extensively used in the computation, the present MRS formalism is not a many-body theory in the conventional sense. Technically this is emphasized in that the summations are performed over determinants rather than orbitals as in diagrammatic perturbation theory [1, 2]. The many-body and the MRS formalisms are both RS theories, and the difference in the summation rule stems from the definition of the reference energy. To see this we must first mention that quasidegenerate RS theory may be formulated by employing [2] dim (p) reference energies instead of one as was done here. These are the dim (p) zeroth-order energies of all p-determinants. The RS series with dim (p) reference energies is obtained from that with one E^0, via an infinite-order summation of a degeneracy-lifting perturbation V_1 acting only in the reference space [2],

$$V_1 = P(H^0 - E^0)P. \tag{7}$$

This transformation affects the convergence properties, as well as the diagrammatic representation, of the quasidegenerate RS series.

On using first-order Feynmann graphs to describe two-electron integrals, it is possible to represent the terms appearing in the many-electron RS series by diagrammatic symbols. These diagrams are classified as either linked or unlinked. If the reference space is complete, i.e. it contains determinants corresponding to all possible occupations of the valence orbitals, then it can be shown by applying the factorization theorem [16], that the unlinked diagrams in a multi-reference-energy series mutually cancel at every order [1, 2]. The diagrammatic representation of the multi-reference-energy RS series is therefore linked for a complete reference space [2]. In this version of the RS series, usually referred to as many-body perturbation theory, summation over q-determinants is replaced by summation over orbitals through the use of linked diagrams. In contrast, the diagrammatic expansion, obtained using a single reference energy for a complete nondegenerate reference space, may include unlinked diagrams. The reason is that under these conditions the factorization theorem [16] may not always hold. Both linked and unlinked diagrams enter the single-reference-energy RS series for a quasidegenerate reference space. Clearly, in this case there is no practical advantgage in replacing the summation over q-determinants by summation over orbitals.

It may seem that since the quasidegenerate single-reference-energy RS series contains unlinked terms, it is not a size-consistent expansion. This is definitely not the case, and the single-reference-energy RS series is order-by-order a proper size-consistent expansion. We can argue for this statement in two ways. First, one might say that it comes about by definition, since, in every order the expansion includes all the unlinked terms, which would have mutually cancelled out if the reference-space degeneracy-lifting terms were summed to infinite order. Observe that problems of size-consistency arise precisely when terms of given order are missing from the expansion. For example, a detailed analysis of the SDCI result in terms of the RS series [6, 7], shows that fourth- and higher-order unlinked terms involving quadruple and triple excitations are absent from the expansion, whereas the analogous terms involving singles and doubles are summed to infinite order (upon diagonalization). This is clearly not the case with the single-reference-energy MRS series which *in every order contains all the* RS *terms* (*linked and unlinked*). It is thus a size-consistent expansion. We arrive at the same conclusion also from the following argument. The degeneracy-lifting operator is manifestly a one-electron operator. Choosing E^0 to be the zeroth-order energy of a reference determinant, say Φ_0, V_1 can always be written as

$$V_1 = \sum_{\substack{i \in p \\ j \in 0}} (\varepsilon_i - \varepsilon_j) c_i^\dagger c_j. \tag{8}$$

Here $c_i^\dagger(c_i)$ is the creation (annihilation) operator of an electron in orbital ϕ_i of energy ε_i; the index i runs over the orbitals occupied in the reference space, while j is restricted to the orbitals of Φ_0. Hence, the transformation from the single-reference-energy series to the linked expansion and vice versa, is essentially equivalent to redefining the orbitals. Such a transformation cannot introduce (or eliminate) a size-consistency error. If the linked expansion is size-consistent so must be the single-reference-energy series.

We now turn to compare the convergence of the two forms of the quasidegenerate

MRS series. Summing the degeneracy-lifting terms to infinite order, brings about the exact cancellation of unlinked terms. However, this may be at the expense of acute problems of divergence. It often happens that the fully linked expansion is divergent because one of the reference determinants is nearly degenerate with a q-determinant called an intruder [17]. There is no physical reason for the latter to be a reference determinant, so that including it in the reference space unnecessarily complicates the calculation. It also may not solve the problem altogether, because the number of such intruders tends to increase on expanding the reference space [9]. As is readily seen, this intruder situation is easily circumvented by using a single reference energy. Simply choose E^0 to be the most isolated zeroth-order eigenvalue amongst the reference space. In short, the single-reference-energy series generally converges better than the linked expansion which has dim (p) reference energies.

Another important advantage of the single-reference-energy series is that it leads to efficient computations. Observe that the three matrices: PVG_0^0VP, $PVG_0^0VG_0^0VP$ and $PV[G_0^0]^2VP$, are no longer hermitian in the multi-reference-energy formulation. In this case all the dim $(p) \times$ dim (p) elements of each matrix have to be computed separately. This means roughly a factor of two in the computational effort as compared with a single-reference-energy computation. This holds true even when diagrams are used, i.e. summation over orbirtals rather than determinants. Furthermore, the fact that the summation unit is q-determinants allows for truncation schemes based on the wave function, which would enhance computations without loss of accuracy [10]. When summing over orbitals truncations are more complicated, since orbitals do not directly relate to the many-electron wave function.

3. Defining the reference space

The main ingredient in the MRS perturbation calculation is the reference space. The basic idea is to improve the results in third (or fourth) order, by expanding the reference space and including the important configurations in the wave function. In many cases it is possible to recognize the relevant configurations on simple physical grounds. Usually there are few such dominant configurations over the interesting range of molecular geometries. Unfortunately, it is also a rule of experience that with small "physical" reference spaces a significant part of the molecular correlation energy is unaccounted for in third-order calculations [9]. The reason is that on the average, small "physical" reference spaces constitute about 95% of the electronic wave function and in many cases even less. In Li_2 for example, the configuration $1\sigma_g^2 1\sigma_u^2 2\sigma_g^2$ is only $\sim$90% by weight of the ground state at the equilibrium distance. Now, as the total correlation energy is rather large compared with its variation due to molecular formation (molecular correlation energy), then leaving out a configuration of 0.5% weight may lead to significant loss in PES accuracy. In short, in order to define the reference space one must have the ability to estimate the weights of configurations in the wave function of interest. That means computing some reliable (but simple to get) approximations; such as the first-order RS wave function [5].

Given an eigenvalue E^n and an eigenvector Ψ_p^n of H_{RS}^n, the nth-order RS wave function is obtained via the wave operator transformation [18] acting on Ψ_p^n

$$\Psi^n = \Psi_p^n + [E^n - QHQ]^{-1} QV\Psi_p^n = \sum_{i=0}^{\infty} \{[E^n - H^0]^{-1} QV\}^i \Psi_p^n. \tag{9}$$

For properties other than the energy, this expansion is rather well convergent. A reasonable estimation for the weight of given configuration directly interacting with the reference space, may therefore be gotten from the first-order wave function [5],

$$\Psi^1 = \Psi_p^1 + [E^1 - H^0]^{-1} QV\Psi_p^1. \tag{10}$$

Experience from CI calculations [5], and perturbation studies on two-electron systems [9], indicate that the first-order wave function in the Epstein–Nesbet [19] (EN) breakup of the Hamiltonian matrix, is a more reliable approximation than that obtained in the Møller–Plesset [20] (MP) scheme. The procedure is therefore as follows: First one should determine the obvious configurations in the desired wave functions over the relevant range of molecular geometries. The EN first-order wave functions (10) are then computed for the obvious reference space, and the weights of the q-configurations are inspected. Some numerical criterion should be established to distinguish the important q-configurations. In H_2 [9] 0.005 weight was sufficient whereas in Li_2, with a larger correlation energy, the cutoff was reduced to 0.002. The q-configurations passing the weight test should become reference configurations. Physical reasoning must be employed here as well. It often happens that q-configurations with occupied high positive-energy virtuals, attain a relatively large weight due to the finiteness of the basis. Such q-configurations do not describe bound molecular states, and therefore should not become reference configurations [9].

As the molecular geometry is varied, the procedure just described yields the set of configurations that are important for the computation of the entire PES. If this set is small then it is possible to use it as single reference space for the whole PES. A more frequent scenario would however be that a definite computational advantage is gained on discarding the unimportant configurations at every geometry. This should be done cautiously, not to affect the shape of the PES (say causing it to be bumpy). The configurations moving back to the q-space must have at the specified geometry, a negligible contribution to the first-order wave function as well as the energy. Removing a p-determinant that is unimportant in the first-order wave function, but which has a significant interaction with the reference space, is likely to introduce an undesired deformation to the PES. This is because a third-order calculation may never recover the interaction, that is fully accounted for in first-order with the removed p-determinant.

4. Numerical selection of q-determinants

The number of operations in the construction of any H_{RS}^n grows quadratically along with the expansion of the reference space. Simultaneously the number of

q-determinants increases with every added reference determinant. Clearly, not all q-determinants are important in the wave function of interest, and many have only a negligible influence on the third-order energy; and as such on any higher-order result. It would therefore make sense to eliminate these "numerically superfluous" q-determinants, thereby reducing the computational effort. A similar procedure is being successfully employed in MRS SDCI calculations [10]. Writing the third-order energy as follows

$$E^3 = \langle\Psi_p^3|H|\Psi_p^3\rangle + \sum_{i\in q} \langle\Psi_p^3|V|\Phi_i\rangle[E^0 - E_i]^{-1}\langle\Phi_i|VG_0^0V|\Psi_p^3\rangle, \tag{11}$$

one sees that if $\langle\Psi_p^3|V|\Phi_i\rangle[E^0 - E_i]^{-1}$ is small, then the contribution of Φ_i may be neglected. The reason is that in a well defined reference space, when convergence is granted, $\langle\Psi_p^3|V|\Phi_i\rangle$ is bigger in magnitude than the second-order interaction $\langle\Phi_i|VG_0^0V|\Psi_p^3\rangle$. Now $\Psi_p^1 \approx \Psi_p^3$ when the reference space includes all the important configurations [5]. Thus, on inspecting the coefficients β_i,

$$\beta_i = \langle\Psi_p^1|V|\Phi_i\rangle[E^0 - E_i]^{-1}, \tag{12}$$

it is possible to assess which q-determinants can be eliminated from the calculation, without significantly altering the overall third-order result. Of course the selection process requires an a priori cutoff criterion, $\beta_{\min}$, which may be estimated from trial calculations. The procedure is therefore as follows: First the reference space is selected according to the guidelines given in Sect. 3. Then the coefficients β_i are computed and those that in absolute value are less than the cutoff $\beta_{\min}$ are singled out. The corresponding elements in the *PVQ* matrix are eliminated. The perturbation calculation then proceeds with the trimmed *PVQ* matrix.

To demonstrate the method, calculations were performed on Li_2 using a [10*s*, 5*p*, 1*d*] gaussian basis set which was contracted to give 52 molecular orbitals in all. The basis consists of Huzinaga's [21] [9*s*, 4*p*] set and additional *s*, *p*, and *d* functions with exponents: 8.13×10^{-3}, 5.11×10^{-3}, and 1.25×10^{-1}, respectively. The five innermost *s* functions were contracted to one with the atomic coefficients given by Dunning [22]. This basis set is reasonably suitable for the ground state, and presumably (with reduced accuracy) for low excited states. The orbitals were solved in the Silverstone-Yin [23] mean-field potential. In this case the orbitals occupied in the ground-state determinant (i.e., $1\sigma_g$, $1\sigma_u$ and $2\sigma_g$) are the exact closed-shell HF solution whereas the virtuals resemble the orbitals of the excited molecule.

The reference space in the perturbation calculations reported here comprised in all 21 Slater determinants. The corresponding configurations are given in Table 1. This reference space constitutes ~98% by weight of the first-order ground-state wave function at 5.0 and 17.0 bohr, and more than 95% of the first excited ${}^1\Sigma_g^+$ and $1^3\Sigma_g^+$ functions. Observe that the first-order weights are quite similar to the exact frozen-core weights (Table 1) obtained from a valence CI with all the excitations out of the $2\sigma_u$ orbital. This supports the credibility of the first-order wave function as means to identify the important configurations. Table 2 gives the RS series to third order (including the [2/1] approximant) in the EN [19]

Table 1. Reference configurations and their weights[a] in the ground-state valence CI (Ψ_v) and first-order EN (Ψ^1) wave functions

	$R = 5.0$ bohr		$R = 17.0$ bohr	
Configuration[b]	$\lvert\Psi_v\rvert^2$	$\lvert\Psi^1\rvert^2$	$\lvert\Psi_v\rvert^2$	$\lvert\Psi^1\rvert^2$
$2\sigma_g^2$	0.905	0.885	0.469	0.476
$3\sigma_g^2$	0.007	0.008		
$2\sigma_u^2$	0.009	0.010	0.469	0.471
$1\pi_{x,u}^2$	0.023	0.029		
$1\pi_{y,u}^2$	0.023	0.029		
$2\sigma_g^1 3\sigma_g^1$			0.013	0.012
$2\sigma_g^1 4\sigma_g^1$			0.019	0.015
$2\sigma_u^1 3\sigma_u^1$				
$2\sigma_u^1 4\sigma_u^1$			0.010	0.007
$1\pi_{x,u}^1 2\pi_{x,u}^1$	0.003	0.003		
$1\pi_{y,u}^1 2\pi_{y,u}^1$	0.004	0.004		
$1\pi_{x,u}^1 3\pi_{x,u}^1$	0.003	0.003		
$1\pi_{y,u}^1 3\pi_{y,u}^1$	0.004	0.004		
Total	0.981	0.975	0.980	0.981

[a] The weight of a configuration is the sum of the weights of the correspondig determinants. Weights less than 0.002 are not shown

[b] Core occupancy in all configurations is $1\sigma_g^2 1\sigma_u^2$

Table 2. Electronic energies[a] obtained from the RS series with the full q-space determined by the reference space of Table 1

	$X\,^1\Sigma_g^+$	$1\,^3\Sigma_g^+$	$2\,^1\Sigma_g^+$
		$R = 5.0$ bohr	
MP_1	−16.693711	−16.611536	−16.587394
MP_2	−16.756165	−16.673195	−16.652163
MP_3	−16.757372	−16.679642	−16.657196
$MP_{[2/1]}$	−16.757396	−16.680396	−16.657621
EN_2	−16.756497	−16.673573	−16.652627
EN_3	−16.758128	−16.679702	−16.657262
$EN_{[2/1]}$	−16.758171	−16.680374	−16.657617
		$R = 17.0$ bohr	
MP_1	−15.390247	−15.318521	−15.313676
MP_2	−15.444812	−15.375266	−15.371438
MP_3	−15.449700	−15.383547	−15.378881
$MP_{[2/1]}$	−15.450181	−15.384962	−15.379983
EN_2	−15.446536	−15.376686	−15.372803
EN_3	−15.450069	−15.383783	−15.379172
$EN_{[2/1]}$	−15.450306	−15.384769	−15.379941

[a] In hartree

and MP [20] breakups of the Hamiltonian matrix, at the internuclear separations 5.0 and 17.0 bohr. In Table 3 the differences Δ_5^{17} between the Born-Oppenheimer energies at 17.0 and 5.0 bohr are compared with the valence CI results and the accurate computations of Schmidt-Mink et al. [24]. For the ground state Δ_5^{17} should be a good approximation to the dissociation energy D_e.

The electronic energies shown in Table 2 were obtained from a full third-order calculation involving all the six electrons. With the basis set used, the maximum number of single and double excitations from a reference determinant is 4421. The total number of q-determinants entering the calculation is 57 169. These are classified as valence, core, and valence-core excitations. Note that on the average, each p-determinant contributes ~2700 distinct excitations. This means that numerous triple and quadruple excitations are introduced on expanding the reference space. This is of course only a small portion of the triple and quadruple sets, notwithstanding the important ones.

The contribution of core-core double excitations to the total correlation energy is roughly two thirds. In particular it has a pronounced effect in second order. Consequently the third-order corrections are rather small as compared with the second-order term (~1/60 for the ground state). Also, the [2/1] Páde approximant is hardly any improvement over the third-order result. This is manifested in the dissociation energies which are better in third order (Table 3). The effect of large core correlations appears also in the discrepancy between the third-order EN and MP ground-state energies at 5.0 bohr. Presumably, the corresponding MP expansion is slower convergent because of the large diagonal core terms. This discrepancy widens when the reference space is reduced in size. Also, the ground-state D_e becomes smaller and further away from the experiment. The core correlations are better accounted for in a larger space where more triple and quadruple excitations effectively enter the computation. Notice that, as expected, the excited-state series are less sensitive to the core correlations. The discrepancies between the third-order EN and MP energies are smaller than for the ground state, and the corresponding Δ_5^{17}'s are closer to those reported by Schmidt-Mink et al. [24].

Table 3. Differences in Born-Oppenheimer energies[a] (Δ_5^{17})

Source	$X\,{}^1\Sigma_g^+$	$1\,{}^3\Sigma_g^+$	$2\,{}^1\Sigma_g^+$
MP_1	0.03288	0.02243	0.00313
MP_2	0.04076	0.02734	0.01014
MP_3	0.03708	0.02551	0.00773
$MP_{[2/1]}$	0.03661	0.02485	0.00705
EN_2	0.03937	0.02630	0.00924
EN_3	0.03747	0.02533	0.00750
$EN_{[2/1]}$	0.03728	0.02502	0.00709
valence CI	0.03720	0.02439	0.00563
Ref. [24]	0.03848	0.02617	0.00791

[a] In hartree

Table 4. Number of excitations in truncated q-spaces[a]

Breakup	$\beta_{\min} = 10^{-8}$	$\beta_{\min} = 10^{-9}$	$\beta_{\min} = 10^{-10}$
		$R = 5.0$ bohr	
MP	7595	16608	30479
EN	7579	16147	29885
		$R = 17.0$ bohr	
MP	5563	10696	16225
EN	5589	10584	16103

[a] The full q-space consists of 57169 determinants

Table 5. The deviation[a] of the ground-state electronic energy obtained with truncated q-spaces from the full q-space limits given in Table 2

$\beta_{\min}$:	10^{-8}	10^{-9}	10^{-10}
		$R = 5.0$ bohr	
MP_2	0.000217	0.000035	0.000003
MP_3	0.000253	0.000037	0.000001
EN_2	0.000207	0.000034	0.000003
EN_3	0.000249	0.000039	0.000001
		$R = 17.0$ bohr	
MP_2	0.000154	0.000018	0.000003
MP_3	0.000203	0.000027	0.000002
EN_2	0.000147	0.000018	0.000002
EN_3	0.000195	0.000027	0.000002

[a] In hartree. All deviations are positive

The majority of the excitations into q-space are valence-core or core type. Interestingly, the result for the ground-state D_e obtained in valence CI with much less excitations, is only slightly less than the full-core third-order EN result. In Li_2 the overall contribution of core correlations to D_e is known to be rather small [24, 25]; ranging between 200 to 400 cm^{-1} depending on the mean-field model. Apparently it is less than the size-consistency error, and thus the full-core SDCI dissociation energy is smaller than the valence CI value in the same basis set [26]. With the Davidson correction [6] the full-core result is near the frozen-core limit. In the expanded reference space used, the third-order perturbation calculation gives directly a D_e comparable to the valence CI result. This is because perturbation theory is inherently a size-consistent method.

Table 4 compares the q-spaces obtained by applying different cutoff criteria on the β_i's computed for the ground state. Tables 5 and 6 depict the errors in the electronic energies of the ground and excited triplet states computed with these truncated q-spaces. The errors are measured relative to the full q-space energies in Table 2. Note that they are always positive indicating that the full q-space values are likely upper bounds.

Table 6. Same as Table 5 but for the lowest-triplet state

$\beta_{\min}$:	10^{-8}	10^{-9}	10^{-10}
		$R = 5.0$ bohr	
MP_2	0.012124	0.003245	0.000359
MP_3	0.013568	0.003643	0.000419
EN_2	0.012074	0.003139	0.000388
EN_3	0.013559	0.003602	0.000471
		$R = 17.0$ bohr	
MP_2	0.006476	0.001933	0.000394
MP_3	0.007926	0.002531	0.000553
EN_2	0.006495	0.001945	0.000388
EN_3	0.007909	0.002527	0.000547

For the ground state, the q-space obtained with $\beta_{\min} = 10^{-9}$ is already sufficiently large to ensure that the third-order energy is as accurate as the full q-space result for all intents and purposes. Even with $\beta_{\min} = 10^{-8}$ the ground state D_e is hardly altered. This is because the truncation errors at 5.0 and 17.0 bohr are both positive and of roughly the same magnitude. The situation is worse for the excited triplet state (Table 6). But this is not surprising because the truncation is based on the first-order ground-state wave function. If instead the excited-state function was used, the situation would have been reversed. It is possible to employ two (or more) functions in the truncation scheme. This would yield a truncated q-space suitable for accurate computations for several states. Of course this truncated q-space would be larger, but not by much. This can be seen from the fact that with $\beta_{\min} = 10^{-10}$ the results for the lowest triplet state are already reasonable (Table 6). Nevertheless, a $\beta_{\min} = 10^{-10}$ ground-state based truncation is not the optimal situation for the excited state. A two-state truncation scheme, with $\beta_{\min} = 10^{-9}$ say, would conceivably produce a smaller q-space than the $\beta_{\min} = 10^{-10}$ ground-state truncation while retaining high accuracy for both states.

The important achievement of the q-space truncation scheme is the savings gained in computing effort (Table 5). Observe that with a full q-space the symmetry-reduced perturbation calculation amounts to the construction of 28 complete SDCI matrices. Ten from the unique diagonal elements, and 18 estimated as the equivalent of 75 distinct off-diagonal ones. Now on using the q-space truncated at the $\beta_{\min} = 10^{-9}$ level, there is an immediate gain of factor five in many operations with practically the same results. Under balanced numerical truncation of the q-space, the perturbation calculation can evidently be performed for large reference spaces at reasonable cost and sufficient accuracy.

5. Summary

We have discussed the implementation of multi-reference-state perturbation theory for the evaluation of potential-energy surfaces. The motivation for doing so is that perturbation theory is inherently a size-consistent method and as such particularly suitable for this purpose. The reference space is a degree of freedom of the theory that gives it the capacity to yield highly accurate surfaces. An organization of the computation to third-order has been presented along with a brief description of the algorithms. Although it is clear that the present codes could be improved on, by invoking parallel processing, and perhaps on using the unitary group [11-13] and other approaches [14, 15], it is also clear that the method is a practical one. An important advantage of the theory is the ability to truncate the determinant space wisely, gaining large savings in computer sources but without sacrificing the accuracy of the surface.

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