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Derivation and pilot application of a scheme for intermediate Hamiltonians in Fock space

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Abstract. A Fock space formulation of the intermediate Hamiltonian approach is derived by introducing shift operators in the equations determining effective Hamiltonians in Fock space. A non-hermitian intermediate Hamiltonian is constructed from the Fock space Bloch equation. An alternative derivation, based on a similarity transformation expression, is presented providing access to hermitian intermediate Hamiltonians. In a pilot application, the potential curves of the two lowest $^1\Sigma_g^+$ states of the H_2 molecule are calculated demonstrating the applicability of the scheme.

1. Introduction

It has been clear for some time that *ab initio* calculations of excited atomic and molecular states using effective Hamiltonian (H_{eff}) theories (for review articles see e.g. [1–5]) suffer from a convergence problem [6] – commonly termed as "intruder states problem" – quite independent of which specific formalism is applied. In applications of the theory of effective Hamiltonians in Fock space [7–10] we have encountered these difficulties too, and as a first step we tried to circumvent the convergence problems by using incomplete model spaces (IMSs) [11–14] instead of complete model spaces (CMSs). This has been successful to some extent [13, 14], especially for atomic excited states [14] (for results of other groups using IMSs on this line, see [15, 16]), but for potential energy surfaces (PESs) of excited molecular states the situation is still unsatisfactory. Even if basis sets of good quality are applied and if the whole potential curve is to be calculated, for diatomic molecules an incomplete model space usually has to be changed somewhere on the potential curve because of convergence difficulties, at least for states of the highest symmetry. This problem was also encountered by Kaldor [17] in a recent investigation of the Li_2 molecule applying a specific form of the open-shell coupled-cluster method (reviewed in [1, 5]). For tri and higher atomic molecules those convergence problems become more and more pronounced.

Malrieu et al. [8] have proposed overcoming the intruder states problem by modifying the H_{eff} formalism [19, 20, 4] to a so-called "intermediate Hamiltonian" approach. In this scheme, formulated in Hilbert space (for a fixed particle

number), the model space (MS) is divided into two subspaces, the "main" and the "intermediate" MS, and only those eigenvalues of the intermediate Hamiltonian which are associated with the main MS ("main eigenvalues" for short), are required to correspond to eigenvalues of the true Hamiltonian H. The eigenvalues associated with the intermediate MS ("intermediate eigenvalues" for short) are, in principle, arbitrary but are determined in a way that avoids intruder problems. Malrieu et al. [18] have derived a perturbation expansion for their intermediate Hamiltonian containing a shift parameter, and the scheme has been applied in this form to the Li_2 molecule [21] and the Be atom [22]. Very recently, transition moments have been calculated using this scheme [23], and the theory has been further developed by Heully et al. [24].

An intermediate Hamiltonian scheme in Fock space, without shift parameters, based on the open-shell coupled-cluster formalism (see e.g. [1, 5]), has been proposed by Mukherjee [25] some time ago. Another suggestion of Mukherjee [26] has been to add a shift operator H_0' to the zeroth order Hamiltonian H_0 given by the usual decomposition

$$H = H_0 + V \tag{1.1}$$

The purpose of the shift operator H_0' which contains a projector onto the intermediate MS, is to shift down the intermediate eigenvalues thus generating a sufficient energy gap between the MS and the virtual space. Due to the nature of the projector, this scheme can be applied only in a Hilbert space for a fixed particle number. There is, nevertheless, some relationship between this idea and the Fock space formalisms in the present work.

The derivations of the intermediate Hamiltonian methods mentioned above have in common that the (generalized) Bloch equation is manipulated following a principle that might be called the "concept of compatible manipulations". By this we mean that for the "main eigenvalues" the manipulations, e.g. the introduction of additional terms, should not destroy the equivalence of the operator equation with the Schrödinger equation. This general concept will also be followed in the present work.

The scheme for an intermediate Hamiltonian in Fock space presented here is formulated in the framework of the "effective Hamiltonians in Fock space" formalism as introduced by Kutzelnigg [7–10]. We briefly review the notation to be used later on, for detailed definitions see [7–12]. Using a compact tensor notation, an arbitrary spin-conserving operator A containing k-particle components A_k is written in second quantization as [7, 10]

$$A = A_s + A_1 + A_2 + \cdots = A_s + A^P_Q E^Q_P + \tfrac{1}{2} A^{PQ}_{RS} E^{RS}_{PQ} + \cdots \tag{1.2}$$

with the Einstein summation convention implied and $P, Q, \ldots$ representing arbitrary spinfree orbitals. In this notation, A_s is a scalar part (a multiple of the Fock space unit operator), the $E^Q_P, E^{RS}_{PQ}, \ldots$ are spinfree one-body, two-body, ... excitation or substitution operators, and their coefficients $A^P_Q, A^{PQ}_{RS}, \ldots$ are spinfree matrix elements defined as [7, 9, 10]

$$\begin{aligned} A^P_Q &= \langle Q|A_1|P\rangle \\ A^{PQ}_{RS} &= \langle RS|A_2|PQ\rangle = \langle R(1)S(2)|A_2(1,2)|P(1)Q(2)\rangle \\ &\vdots \end{aligned} \tag{1.3}$$

The spins α and β are summed over, in the substitution operators, in such a way

that spin is conserved in each electron coordinate [7, 9, 10]

$$E_P^Q = \sum_{\eta=\alpha}^{\beta} a_{Q\eta}^{\dagger} a_{P\eta} \quad (=: a^{Q\eta} a_{P\eta} =: a_{P\eta}^{Q\eta})$$

$$E_{PQ}^{RS} = \sum_{\eta,\,\xi=\alpha}^{\beta} a_{R\eta}^{\dagger} a_{S\xi}^{\dagger} a_{Q\xi} a_{P\eta} \quad (=: a^{R\eta} a^{S\xi} a_{Q\xi} a_{P\eta} =: a_{P\eta Q\xi}^{R\eta S\xi})$$

$$\vdots \tag{1.4}$$

with $a_q^{\dagger}$ and a_p being the usual creation and annihilation operators for spin orbitals. The particular spin summation in Eqs. (1.4) takes care of the original spin dependency of the matrix elements built from spin orbitals.

The operator space is divided into various sets, and aiming at being as general as possible, we use the definitions appropriate for both the CMS and the IMS case [7–12]: 'Diagonal' operators (index 'D') cannot excite from the MS, but 'Non-diagonal' ones (index 'N') can do so. 'Closed' operators (index 'C') act on MS functions, and map them only onto MS functions again. The category 'N' consists essentially of operators of 'B'-type ('closed from Below') being able to excite from the MS, and for a unitary ansatz [7, 8], also of operators of 'A'-type ('closed from Above') which act in the opposite direction. Generally, in this classification a hierarchy principle is implicit: 'N' has the highest priority, followed by 'C'. Hence, the category 'D' comprises operators of the following types: operators of type 'C', and in non-unitary formalisms also of type 'A', and additionally all remaining operators not in 'N', which are termed 'Open' (index 'O'). 'O' operators always give zero if applied to MS vectors from the left, as well as to their conjugates from the right. Note that in other formalisms [1, 5] 'B' operators are called 'open', and 'O' operators do not appear. Scalars, like the Fock space unit operator or vacuum terms, belong in principle to the separate category of scalars [8], but for convenience we mostly subsume them in the 'C' category.

Following Kutzelnigg [7–10] the wave operator and the effective or intermediate Hamiltonian in Fock space are denoted as W and L_C respectively, where L_C is the closed part of the diagonal "energy operator" L [7–10]. Similar to H, the operator L is decomposed into

$$L = H_0 + \Delta L \tag{1.5}$$

The operator classification briefly described above is related to the (full) MS, but for the intermediate Hamiltonian schemes we will additionally need the same kind of operator classification but related only to the main MS. To avoid subindexing of indices, this classification is simply indicated by adding an index m to the indices introduced above, hence an operator A closed with respect to the main MS is denoted as A_{Cm}. For functions and scalars, the index m will be simultaneously used as counting index.

If we use the term "model space" we do not mean only the space spanned by the selected active configuration state functions for a specific particle number n, but also for other particle numbers as outlined in [7–12]. Naturally the same holds for the complementary space, called the virtual space in what follows, and for the main and intermediate MS. However, we would like to stress that the schemes presented in this work are not only applicable in Fock space, but also in

Hilbert space, be it by projection of the equations to a particular n-particle Hilbert space or via an interpretation of the operators as pure Hilbert space operators.

2. Construction of an intermediate Hamiltonian in Fock space from the Bloch equation

In this paper a Fock space intermediate Hamiltonian scheme having the following characteristics is presented:

(i) individual orbital energy shifts are applied to ensure that energy denominators are always sufficiently large

(ii) the feature of particle-number independence is conserved

(iii) connectivity can probably be maintained.

To reach goal (i) we shall enlarge the energy denominators related to the intermediate MS. Hence, depending on the energy range of the main MS, the intermediate MS has to be chosen sufficiently large to act as a "buffer space" between the main MS and the virtual space. Point (ii) can be fulfilled by formulating all equations strictly in Fock space in the sense of [7–12] which will also help to realize item (iii). Connectivity will not be discussed here in detail, proofs for it have to be given elsewhere.

Shifts are most easily introduced starting from the (generalized) Fock space Bloch equation [7, 8]

$$HW = WL, \quad L = L_D \tag{2.1}$$

with some ansatz for the wave operator generally resulting in a non-hermitian L_D. The model space to which the index 'D' refers, may be complete or incomplete (CMS or IMS case).

From Eq. (2.1), we first generate a new energy operator $\tilde{L}$ via a transformation with a Fock space operator B such that $\tilde{L}$ is 'diagonal with respect to the main MS' indicated by the double index 'Dm':

$$HWB = WBB^{-1}LB = WB\tilde{L}, \quad \tilde{L} = \tilde{L}_{Dm} \tag{2.2}$$

(Note that the unit operator is an essential part of B, as it is for any similarity transformation.) If, as mentioned, the unit operator is for convenience subsumed in the 'C' category, it is even possible to restrict B to be a closed operator because only operators that couple the main and the intermediate MS have to be removed by B, and these operators are parts of L_C only. Even if B is constructed via an exponential(-like) expansion with a closed operator as exponent, B will still be closed for a CMS since there the "multiplication rule", that a product of two closed operators results in a closed operator again ('$C \times C = C$') [8], holds. This also ensures that B^{-1} is closed. For an IMS [11, 12] that rule is valid only for operators of a fixed particle rank, otherwise one has to relax the rule to '$C \times C = D$' (see below). We will see, however, that non-closed diagonal components in B do not cause problems. Hence, if necessary, one could extend B to $B = B_D$.

It would not be possible to restrict B to $B = B_C$ (or $B = B_D$) if, in the decoupling expression $B^{-1}LB$, non-diagonal terms could appear belonging to both the 'N' and 'Nm' sets. To have the condition $\tilde{L} = \tilde{L}_{Dm}$ fulfilled, those

operators would have to be additionally removed by B. For the CMS case the multiplication rule '$D \times D = D$' [8] was formulated, which ensures in this case that the decoupling expression is diagonal, since the three operators in the product are diagonal. For the IMS case [11, 12] that multiplication rule was not explicitly stated, but, from the general definition that a diagonal operator cannot excite any MS function to a virtual function, we can easily conclude that a product of two diagonal operators cannot do this either. Hence that multiplication rule is valid for the IMS case too, and we have the result that generally no 'N' terms can appear in the decoupling expression. Put differently, the condition $L = L_D$ is preserved if B is chosen to be a closed operator; $\tilde{L} = \tilde{L}_D$ holds as well.

The right hand side (r.h.s.) eigenfunctions of the new effective Hamiltonian $\tilde{L}_{Cm}$ generated by Eq. (2.2) are spanned by basis functions of the main MS ("main functions") only, and it is compatible with conserving the pertinent eigenvalues (the only eigenvalues in which we are interested) to add operators in Eq. (2.2) that give zero when acting on main functions. Introducing a shift operator D with this property, one of the (in principle) infinite possibilities to modify Eq. (22) is (with $\tilde{W} = WB$)

$$H\tilde{W} = \tilde{W}\tilde{L} + X_N BD, \quad \tilde{L} = \tilde{L}_{Dm} \tag{2.3}$$

In one possible choice, X_N is the non-diagonal part of W, i.e.

$$X_N = W_N \tag{2.4a}$$

For theories using a cluster expansion [1, 5] for W, e.g.

$$W = \exp S, \quad S = S_N \tag{2.4b}$$

in coupled cluster theory [1, 5, 7–13] or

$$W = \exp \sigma, \quad \sigma = \sigma_N, \quad \sigma^\dagger = -\sigma \tag{2.4c}$$

in the separable unitary ansatz as advocated by Kutzelnigg [7–13], it is convenient to define X_N in terms of these cluster operators, i.e.

$$X_N = S \quad \text{or} \quad X_N = X_B = \sigma_B \tag{2.4d}$$

respectively. In Eq. (2.3) and in the following, we always demand that X_N is connected with D – directly or through B – (and, for safety, that B is connected with D), because the idea is that the additional term will finally contribute to the commutator of X_N with H_0. The insertion of the operator B between X_N and D in Eq. (2.3) is not really needed, the motivations for inserting it will be given below. In any case, we would like to stress the flexibility in the choice of the shift term. It is, e.g., possible to restrict X_N to certain parts of W_N, S, σ etc., or to restrict the whole shift term, e.g., to $(X_N BD)_N$. This variability will help to adapt the formalism to the peculiarities of a specific application.

By introducing the extra-term in Eq. (2.3), it is intended to lower the energies of orbitals appearing in "intermediate functions", i.e. functions spanning the intermediate MS, and therefore we define D to be a shift operator acting on intermediate functions. In particular we choose D to be of the "index-diagonal" form

$$D = D_X E_X^X + \tfrac{1}{2} D_{XY} E_{XY}^{XY} + \cdots \tag{2.5}$$

where X, $XY, \ldots,$ are (sets of) active orbitals appearing in intermediate functions, but not in main functions. Obviously, demanding D to be a Fock space operator introduces the restriction in the choice of main and intermediate

MS that the two subspaces have to differ in the occupation of certain orbitals or orbital sets. In Hilbert space, or if one likes to work with a projection of the Fock space equations to a particular n-particle Hilbert space, such a restriction is not necessary since D can be simply defined to project onto the intermediate MS. However, in practice, it should normally be no problem to construct a main and intermediate MS accordingly. The shift operator D is required to be of low particle rank, since its purpose is to help solving the k-particle operator equations, usually with $k = 1, 2, 3, 4$ (plus n-particle-m-hole equations if a core is correlated), where $k = 2$ is normally of central importance. Hence, in the intermediate MS, energetically high lying orbitals or orbital pairs acted upon by D, which are unoccupied or only singly occupied in the main MS, should be populated. On the contrary, it is often favourable if some low lying orbitals are always doubly or at least singly occupied in the main MS. All of these conditions can probably be best realized by choosing an appropriate IMS as the full MS, whereas it might be difficult to subdivide a CMS using those criteria. It may be helpful to additionally use shift operators defined in a complementary way, i.e. "acting on vacancies". The operator $\bar{D}_Z(1 - E_Z^Z + E_{ZZ}^{ZZ})$, e.g., acts only on functions in which the orbital Z is *un*occupied. Summarizing it can be said that applications of this Fock space formalism will often require a somewhat larger MS than it would be necessary if projectors were used.

To demonstrate explicitly that the shift term in Eq. (2.3) – to be classified as an '*Om*' or '*Am*' term – does not change the main MS eigenvalues, we apply Eq. (2.3) to an eigenfunction $\tilde{\Phi}_m$ of $\tilde{L}_{Cm}$:

$$H\tilde{W}\tilde{\Phi}_m = \tilde{W}\tilde{L}\tilde{\Phi}_m = \tilde{W}\tilde{L}_{Cm}\tilde{\Phi}_m = \tilde{W}E_m\tilde{\Phi}_m \tag{2.6}$$

This shows that Eq. (2.3) is still equivalent to the Schrödinger equation for main eigenvalues, with wave functions $\tilde{W}\tilde{\Phi}_m$. However, one should realize that for the manipulated Eq. (2.3) to hold, the matrix elements of all variable operators will generally have to change. Hence, in principle, for these operators a different notation (like $\tilde{W}'$, $\tilde{L}'$) should have been used from Eq. (2.3) onwards, but for simplicity we will continue to use the old one.

Now we recover an equation for W and L similar to the Bloch Eq. (2.1) by multiplying Eq. (2.3) with B^{-1} from the r.h.s.:

$$HW = WL + X_N BDB^{-1}, \quad L = L_D \tag{2.7}$$

This remarkably simple equation generates the intermediate Hamiltonian L_C as used in this work. Equation (2.7) might be referred to as the "shifted Bloch equation".

The (closed) term BDB^{-1} is hoped to be similar to D in structure, whereas DB^{-1} is probably quite different, and this is the main reason why B was inserted into the shift term in Eq. (2.3). The other reason is that BDB^{-1} may be nearly hermitian if the unshifted L_C is (if it could be calculated), and hence it is hoped that the specific form of the shift term in Eq. (2.7) will prevent the intermediate Hamiltonian from becoming strongly non-hermitian.

Since, at least for a CMS, the shift term is purely of 'N' type (any explicit 'D' component would be more or less compensated through the back-substitution of L), Eq. (2.7) recovers the usual expressions for ΔL_C in the CMS case, e.g. in intermediate normalization [7, 8]

$$\Delta L_C = (VW)_C \tag{2.8}$$

whereas the equation that determines X_N now reads

$$[X_N, H_0] + X_N D = (VW)_N - (W\,\Delta L)_N - (X_N(BDB^{-1} - D))_N \tag{2.9}$$

The internal structure of the terms in Eq. (2.9) is not indicated, since that is determined by the specific ansatz chosen for W. The "simple shift term" $X_N D$ on the l.h.s. of Eq. (2.9) was extracted from the shift term in Eq. (2.7), leaving a "shift correction term" placed as the last term on the r.h.s. of Eq. (2.9). Note that the shift operator D appears only on the r.h.s. of X_N.

The specific intermediate Hamiltonian method defined by Eqs. (2.7) or (2.8, 9) will be referred to as "scheme a" in this work. Equation (2.9) may be looked upon as containing simple shifts that provide sufficiently large energy denominators, and a shift correction term which corrects the resulting errors with respect to those energies that are not directly affected by the shifts. Hence a simple approximation to scheme a consists in keeping only the simple shift term, i.e. dropping the shift correction term on the r.h.s. of Eq. (2.9):

$$[X_N, H_0] + X_N D = (VW)_N - (W\,\Delta L)_N \tag{2.10}$$

This approximation, with the expression for ΔL_C unchanged, is denoted as "scheme b", and both schemes a and b are tested in the numerical application.

Obviously, in the solution of Eqs. (2.8, 9) the critical point is the determination of the B into which the intruder problem has been absorbed. B is conveniently calculated from the decoupling expression $B^{-1}LB$, already discussed above, using the condition

$$(B^{-1}LB)_{Nm} = ((B^{-1}LB)_C)_{Nm} = 0 \tag{2.11}$$

to which essentially only L_C contributes. In constructing B from Eq. (2.11) perturbation theory or methods related to it generally cannot be used since a helpful energy gap between main and intermediate MS cannot be expected to exist. Instead, numerically stable iterative methods have to be applied, which should be possible because the MS is assumed to be sufficiently small. Determining B iteratively generally implies that L_C will be determined iteratively, too, and in every iteration cycle the operators W, L_C and the pertinent B have to be calculated until selfconsistency is reached.

The problem of arriving at a connected L_C will not be specifically addressed here, since this is a trivial point for the two-electron example presented below. In this paragraph, however, we will make at least a few remarks on this topic to indicate how connectedness of L_C can be achieved and proved in a transparent way using the Fock space methodology developed so far [7–12]. Though the shift operator D is not directly a part of H or L, it has a position in the equation for X_N which makes it look like a part of L_C. Hence, there is some reason to demand D to be additively separable like H or L, so that according to the separability theorem as advocated by Kutzelnigg [7, 10], D can be considered to be connected. In practice, additive separability of D can simply be realized if one defines the coefficients in D to approach some constant asymptotic values for any dissociative coordinate. Furthermore, it must be possible to compose these values additively from reasonable shifts for the separate systems calculated individually. Then, to achieve multiplicative separability of W, X_N may be chosen to be an additively separable cluster operator connected with D. Finally, what is left to be considered is the connectedness of the expression BDB^{-1} in Eq. (2.9). If we choose an exponential(-like) ansatz for B, in the same way as is usually done for W [1, 5, 7–13], it should be possible to make this expression

connected and hence to arrive at connected-diagram expansions for the cluster operator X_N and the intermediate Hamiltonian L_C. It will become more apparent in the next section that B plays a role similar to W.

The shifts in Eqs. (2.7, 9) cannot usually be chosen as fixed on a potential energy surface (PES), because for PESs of excited states the intruder problem is aggravated by the fact that generally, in different areas of the PES, different MS configurations get intruded to a variable extent (by possibly different virtual states). In principle, this still could simply be circumvented by choosing the MS to be sufficiently large and always shifting all the configurations that get intruded somewhere. In applications, however, there are practical limitations to the size of the MS, and experience has shown that usually, somewhere on the PES, a few of the shifted configurations are dominant in the states of interest (and hence should not be shifted). We suggest overcoming this difficulty by switching the various shifts on and off as needed, and furthermore to do this continuously in order to avoid kinks in the PES. A main advantage of this intermediate Hamiltonian formalism is that the MS, if appropriately chosen, does not need to be changed in course of a PES calculation, as e.g. had to be done in [17] for the two lowest Li_2 $^1\Sigma_g^+$ states causing slight discontinuities in their potential curves.

3. Construction of intermediate Hamiltonians via similarity transformations (non-unitary and unitary)

Since the derivation of the intermediate Hamiltonian scheme via the Bloch equation required a decoupling transformation in the MS (by the operator $B = B_C$), it is now clear how the same results can be obtained via a two step similarity transformation, i.e., defining L at the outset by a similarity transformation [7, 8, 10], instead of using the Bloch equation for the definition of L. This is of general theoretical interest, and had been an unsolved problem. This starting point is even mandatory for the formulation of an intermediate Hamiltonian scheme in the framework of the unitary ansatz as proposed by Kutzelnigg [7, 8, 10], which is essentially based on an unitary transformation expression defining L (see below).

Starting from the transformation in Fock space that creates the decoupled energy operator L [7, 8, 10]

$$W^{-1}HW = L, \quad L = L_D \tag{3.1}$$

a second similarity transformation, using $B = B_C$, is applied to construct the operator $\tilde{L}$ with the properties as described in Sect. 2:

$$B^{-1}W^{-1}HWB = B^{-1}LB = \tilde{L}, \quad \tilde{L} = \tilde{L}_{Dm} \tag{3.2}$$

Using the arguments from the previous section, it is compatible with conserving the eigenvalues of $\tilde{L}_{Cm}$ if one adds an operator to Eq. (3.2) which gives zero when acting on main functions. Put in a different way, the conditions

$$(\tilde{W}^{-1}H\tilde{W})_{Cm} = \tilde{L}_{Cm} \tag{3.3a}$$

$$(\tilde{W}^{-1}H\tilde{W})_{Nm} = 0 \tag{3.3b}$$

(with $\tilde{W} = WB$) should be preserved by this manipulation.

In order to arrive at the same result as in the previous section, we now add a convenient operator product, with the shift operator $D = D_{Om} = D_C$ at the

right end which guarantees that the product is of type '*Om*' or '*Am*':

$$B^{-1}W^{-1}HWB = \tilde{L} + B^{-1}W^{-1}X_N BD, \quad \tilde{L} = \tilde{L}_{Dm} \tag{3.4}$$

Multiplication of Eq. (3.4) by WB from the left and B^{-1} from the right finally reproduces Eq. (2.9)

$$HW = WL + X_N BDB^{-1}, \quad L = L_D \tag{3.5}$$

This result demonstrates that scheme *a* can also be derived from an effective Hamiltonian that is defined by a similarity transformation. Below we will proceed in this way for the construction of hermitian intermediate Hamiltonians. However, in contrast to the situation for effective Hamiltonians, it does not seem to be possible to define an intermediate Hamiltonian by a pure similarity transformation expression without additional terms.

In this work, we do not present an application of a hermitian intermediate Hamiltonian, but we at least want to give examples of such intermediate Hamiltonians constructed from an unitary ansatz. The derivation is now based on the unitary transformation [7, 8, 10]

$$W^{\dagger}HW = L, \quad L = L_{\mathrm{D}}, \quad W^{\dagger} = W^{-1} \tag{3.6}$$

that can, e.g., be realized using the separable unitary ansatz [7, 8, 10]

$$W = \exp\sigma, \quad \sigma = -\sigma^{\dagger}, \quad \sigma = \sigma_N \tag{3.7}$$

($X_N = X_B = \sigma_B$ in this case). The main MS is now decoupled applying a transformation with a *unitary* Fock space operator $B = B_C$ (e.g. $B = \exp\tau$, $\tau = -\tau^{\dagger}$):

$$B^{\dagger}W^{\dagger}HWB = B^{\dagger}LB = \tilde{L}, \quad \tilde{L} = \tilde{L}_{Dm} \tag{3.8}$$

As before, we add operators to $\tilde{L}$ that give zero when applied to main functions. To preserve the hermiticity of $\tilde{L}$ and L, we have to add a shift term plus its hermitian conjugate, which restricts the shift term to be of type '*Om*'. The hermitian conjugate term causes problem in the IMS case, hence we first restrict the discussion to the simpler CMS case where '*A*' type operators always give zero when applied to main (and intermediate) functions. Then one possibility is

$$B^{\dagger}W^{\dagger}HWB = \tilde{L} + B^{\dagger}X_B BD + DB^{\dagger}X_B^{\dagger}B, \quad \tilde{L} = \tilde{L}_{Dm} \tag{3.9}$$

($D = D^{\dagger}$ by definition). Here, with respect to the full MS, the first shift term is of type '*B*' and the second of type '*A*'. Back-transformation of Eq. (3.9) yields the equation

$$W^{\dagger}HW = L + X_B BDB^{\dagger} + BDB^{\dagger}X_B^{\dagger}, \quad L = L_D \tag{3.10}$$

defining a hermitian intermediate Hamiltonian L_C. With

$$D' = BDB^{\dagger} \tag{3.11}$$

the pertinent shifted Bloch equation is

$$HW = WL + WX_B D' + WD'X_B^{\dagger}, \quad L = L_D \tag{3.12}$$

Equally, one could start from Eq. (3.12) going backwards to Eq. (3.10) or (3.9).

In the term $WX_B D'$ of Eq. (3.12), the unpleasant part W_O of the operator W contributes, and if one wishes to avoid this, the alternative, somewhat more involved ansatz

$$B^{\dagger}W^{\dagger}HWB = \tilde{L} + B^{\dagger}(W^{\dagger}X_B BD)_B + (DB^{\dagger}X_B^{\dagger}W)_A B, \quad \tilde{L} = \tilde{L}_{Dm} \tag{3.13}$$

may be used for a CMS instead of Eq. (3.9). This leads to

$$W^\dagger HW = L + (W^\dagger X_B D')_B + (D' X_B^\dagger W)_A, \quad L = L_D \tag{3.14}$$

defining another hermitian intermediate Hamiltonian L_C. Using the decomposition

$$(W^\dagger X_B D')_B = W^\dagger X_B D' - (W^\dagger X_B D')_{C,\,O,\,A} \tag{3.15}$$

we can write the pertinent shifted Bloch equation as

$$HW = WL + X_B D' - W(W^\dagger X_B D')_{C,\,O,\,A} - W(D' X_B^\dagger W)_A, \quad L = L_D \tag{3.16}$$

In the relevant components of Eq. (3.16), i.e. the 'B' and 'C' parts, W_O does not contribute.

In the IMS case, equations analogous to those for the CMS case can be used if X_B is restricted to X_{BC} [11, 12], i.e. to that kind of operator that only excites from the IMS to the inactive space that is the complementary space of the CMS in which the IMS is embedded. If one wants to include more components of X_N the following ansatz may be used:

$$B^\dagger W^\dagger HWB = \tilde{L} + (X_B D)_{Om} + (D X_B^\dagger)_{Om}, \quad \tilde{L} = \tilde{L}_{Dm} \tag{3.17}$$

The operator B between X and D has been dropped here since its insertion is probably not of much use in a hermitian formalism. Equation (3.17) is applicable at least in the case where the IMS is isolated [11], but general IMSs [12] can also be included if the non-diagonal '$\pm$' operators [12, 13] typical for general IMSs are symmetrically distributed to the 'B' and 'A' operator sets. This is possible since the '$\pm$' operators always occur in hermitian conjugate pairs [12]. Back-transformation of Eq. (3.17) with B yields

$$W^\dagger HW = L + B(X_B D)_{Om} B^\dagger + B(D X_B^\dagger)_{Om} B^\dagger, \quad L = L_D, \tag{3.18}$$

defining a third hermitian intermediate Hamiltonian L_C which may be determined from the shifted Bloch equation

$$HW = WL + WB(X_B D)_{Om} B^\dagger + WB(D X_B^\dagger)_{Om} B^\dagger, \quad L = L_D \tag{3.19}$$

The way of constructing intermediate Hamiltonians as presented in this section can be characterized as forth-and-back transformation with shifts inserted between the transformation steps. Equations (3.14, 16), interpreted in Hilbert space, may also be useful for CI-problems or generally matrix eigenvalue problems suffering from quasi-degeneracies, as, for these kinds of problems, the equations can be drastically simplified.

4. Pilot application to the H_2-molecule

The excited $^1\Sigma_g^+$ states of the H_2 molecule are chosen as a pilot application for the intermediate Hamiltonian schemes a and b (Eqs. 2.8–10). These states belong to the most difficult test problems for H_{eff} formalisms, at least for medium and large basis sets, because their intruder problems are particularly severe (see e.g. [14, 27]). Taking the smallest non-trivial example, we aimed to calculate the ground and first excited $^1\Sigma_g^+$ states "exactly", and it was found that the MS $(1\sigma_g^2, 1\sigma_u^2, 1\sigma_g 2\sigma_g, 1\sigma_g 3\sigma_g)$ is sufficient to reach convergence over the whole range of internuclear distances, at least up to $R = 8\,a_0$. This MS can be classified as "isolated IMS" [11].

The Schulman–Kaufman basis set of size $(10s, 5p, 1d)$ [28] was used (in uncontracted form; 60 groups) because this basis set is just sufficient to achieve "chemical accuracy" for the two lowest ${}^1\Sigma_g^+$ states of H_2. That basis set, also used by Sawatzki and Cederbaum [27] in investigations of the intruder problem, may be characterized as a "medium size" basis set.

In line with our H_2 calculations in [8, 14], for simplicity the bare nuclear Hamiltonian (BNH) is chosen as zeroth order Hamiltonian H_0, leaving the full electron interaction as perturbation V. The molecular orbitals are generated by diagonalization of H_0, hence the molecular orbital (MO) basis is formed by H_2^+ orbitals. For the wave operator, the normal order ansatz (see e.g. [1, 5])

$$W = \{\exp S\} \tag{4.1}$$

is used in a particle-only framework (no holes) similar as it was done in [13]. With that specific choice of H_0, the cluster operator S does not contain 1-particle operators [8, 14], and for the 2-electron system considered here the ansatz (4.1) is simplified to

$$W = 1 + S_2 \tag{4.2}$$

i.e., the wave operator contains only the unit operator and the 2-particle cluster operator exciting from the MS to outside. The absence of a 1-particle cluster operator is the reason that in this example connectivity of L_C cannot be missed, and that computationally the scheme becomes equivalent to a CI scheme in structure.

In the ground state, $1{}^1\Sigma_g^+$, the dominant configurations are $1\sigma_g^2$ and $1\sigma_u^2$ for large R ($R \gtrsim 5\,a_0$), and $1\sigma_g^2$ for smaller R. The $2{}^1\Sigma_g^+$ state – $EF{}^1\Sigma_g^+$ in spectroscopic notation – is known to have two minima, the inner ("covalent") one at $R = 1.91\,a_0$ associated with the dominant configuration $1\sigma_g 2\sigma_g$, and the outer ("ionic") one at $4.39\,a_0$ associated with $1\sigma_u^2$ (and a large $1\sigma_g^2$ component from the ionic configuration $1\sigma_g^2 + 1\sigma_u^2$) [29]. Both the minima are reproduced by the basis set, though at slightly shifted positions. To illustrate the composition of the states in terms of MO configurations the components of the model functions as calculated with scheme a (scheme b is similar) are listed in Table 1. Near $R = 8\,a_0$, the $2{}^1\Sigma_g^+$ state is again dominated by $1\sigma_g 2\sigma_g$, since the first ionic dissociation channel associated with the configuration $1\sigma_g^2 + 1\sigma_u^2$ is higher in energy than the "covalent" $H(1s) + H(2s, 2p)$ dissociation limit. As becomes apparent from Table 1, extreme configuration mixing happens at large internuclear distances.

Thus, at least $1\sigma_g$, $1\sigma_u$, and $2\sigma_g$ have to be chosen as active orbitals, and we add $3\sigma_g$ to this set to have $1\sigma_g 3\sigma_g$ as a "buffer configuration" in the intermediate space. (For calculations beyond $R = 8\,a_0$, one would have to include quite a few more configurations.) The dominant configurations of the states of interest, here 1 and $2{}^1\Sigma_g^+$, always comprise the main MS, and all other configurations spanning the intermediate MS are shifted by suitable operators that do not act on main functions. Accordingly, $3\sigma_g$ (i.e. the orbital energy of $3\sigma_g$) is shifted for all R in the equation for S_2, and additionally $1\sigma_u$ is shifted for small internuclear distances and $2\sigma_g$ for larger ones. The shift operator D is chosen to be of the form $D = D_X E_X^X$, with X representing the active orbitals to be shifted.

In every cycle of the iterative calculation of the intermediate Hamiltonian L_C, the configurations of the main and the intermediate MS have to be decoupled from each other by the closed operator B which is assumed to be a 2-particle operator throughout (other than the unit operator). Since one need not

Table 1. Configuration coefficients of the four H_2 $^1\Sigma_g^+$ model states for selected internuclear distances R (in atomic units, a_0, as calculated by the intermediate Hamiltonian scheme a (the figures for scheme b are similar)

R [a_0]	$^1\Sigma_g^+$ States	Coefficients $1\sigma_g^2$	$1\sigma_u^2$	$1\sigma_g 2\sigma_g$	$1\sigma_g 3\sigma_g$
0.8					
	1	0.971	−0.042	0.225	−0.070
	2	−0.118	−0.009	0.767	0.630
	3	0.205	0.020	−0.659	0.723
	4	0.035	0.999	0.027	−0.012
1.4					
	1	0.969	−0.088	0.221	−0.068
	2	−0.121	0.002	0.774	0.621
	3	0.197	0.001	−0.640	0.743
	4	0.085	0.996	0.011	0.001
2.0					
	1	0.963	−0.156	0.210	−0.068
	2	−0.115	0.031	0.789	0.603
	3	0.158	−0.052	−0.589	0.791
	4	0.163	0.984	−0.041	0.057
3.2					
	1	0.920	−0.352	0.159	0.072
	2	0.093	0.515	0.808	−0.271
	3	0.353	0.812	−0.407	−0.225
	4	0.038	0.333	0.093	0.937
4.2					
	1	0.843	−0.521	0.090	0.100
	2	0.439	0.742	0.436	−0.258
	3	−0.237	−0.239	0.936	0.106
	4	0.073	0.299	−0.022	0.951
6.0					
	1	0.745	−0.663	−0.049	0.062
	2	0.573	0.622	0.496	0.197
	3	−0.343	−0.323	0.234	0.851
	4	−0.199	−0.327	0.801	−0.460
8.0					
	1	0.715	−0.698	−0.019	0.030
	2	0.538	0.537	0.641	0.112
	3	−0.424	−0.416	0.432	0.678
	4	0.235	0.289	−0.551	0.747

worry about connectivity in this example, B is simply defined as a matrix in the 2-electron (singlet) space. The procedure of block-diagonalizing L_C, represented as a (non-hermitian) matrix in the 2-electron MS, is somewhat problematic because block-diagonalizing a non-hermitian matrix is not a standard procedure, and moreover the blocking scheme changes when R is varied. To avoid these complications for the time being, L_C, respectively its matrix representation, was

Table 2. Energies (in hartrees, h) of H_2 $^1\Sigma_g^+$ states for selected internuclear distances R (in atomic units, a_0) calculated by the intermediate Hamiltonian scheme a (Eqs. 2.7–9) and the approximate scheme b (Eq. 2.10). Full CI (configuration interaction) values are added for comparison. The states are characterized by their dominant configuration(s). The shift values D_X (in h) are given in the first column in the lines of the configurations that are directly affected by them

	$^1\Sigma_g^+$ States		Energies		
	No.	Conf.	Scheme b	Scheme a	FCI
$R = 0.8\ a_0$					
	1	$1\sigma_g^2$	−1.019784	−1.018922	−1.018922
	2	$1\sigma_g 2\sigma_g$	−0.441895	−0.435991	−0.435991
$D_{3\sigma g} = -0.740$	3	$1\sigma_g 3\sigma_g$	−0.290732	−0.251083	−0.327342
$D_{1\sigma_u} = -0.680$	4	$1\sigma_u^2$	+0.567239	+0.567709	+0.504837
$R = 1.4\ a_0$					
	1	$1\sigma_g^2$	−1.173995	−1.173249	−1.173249
	2	$1\sigma_g 2\sigma_g$	−0.695629	−0.691501	−0.691501
$D_{3\sigma_g} = -0.612$	3	$1\sigma_g 3\sigma_g$	−0.554435	−0.528094	−0.580145
$D_{1\sigma_u} = -0.228$	4	$1\sigma_u^2$	−0.087494	−0.086824	−0.095686
$R = 2.0\ a_0$					
	1	$1\sigma_g^2$	−1.136870	−1.136548	−1.136548
	2	$1\sigma_g 2\sigma_g$	−0.718347	−0.716931	−0.716931
$D_{3\sigma_g} = -0.183$	3	$1\sigma_g 3\sigma_g$	−0.590561	−0.581751	−0.602381
$D_{1\sigma_u} = -0.064$	4	$1\sigma_u^2$	−0.413814	−0.412772	−0.459420
$R = 3.2\ a_0$					
	1	$1\sigma_g^2$	−1.044299	−1.044290	−1.044290
	2	$1\sigma_g 2\sigma_g$	−0.686288	−0.687712	−0.687712
	3	$1\sigma_u^2$	−0.654395	−0.651871	−0.651871
$D_{1\sigma_g} = -0.520$	4	$1\sigma_g 3\sigma_g$	−0.376962	−0.371656	−0.400045
$R = 4.2\ a_0$					
	1	$1\sigma_g^2$	−1.011638	−1.011611	−1.011611
	2	$1\sigma_u^2$	−0.710072	−0.709140	−0.709140
	3	$1\sigma_g 2\sigma_g$	−0.639636	−0.639056	−0.639056
$D_{3\sigma_g} = -0.300$	4	$1\sigma_g 3\sigma_g$	−0.401969	−0.397889	−0.423087
$R = 6.0\ a_0$					
	1	$1\sigma_g^2, 1\sigma_u^2$	−1.000619	−1.000675	−1.000675
	2	$1\sigma_u^2, 1\sigma_g^2$	−0.694119	−0.688357	−0.688357
$D_{3\sigma_g} = -0.424$	3	$1\sigma_g 3\sigma_g$	−0.574283	−0.550463	−0.618709
$D_{2\sigma_g} = -0.374$	4	$1\sigma_g 2\sigma_g$	−0.447952	−0.440102	−0.480713
$R = 0.8\ a_0$					
	1	$1\sigma_g^2, 1\sigma_u^2$	−0.999944	−0.999979	−0.999979
	2	$1\sigma_g 2\sigma_g, 1\sigma_g^2, 1\sigma_u^2$	−0.658208	−0.654817	−0.654817
$D_{2\sigma_g} = -0.362$	3	$1\sigma_g 3\sigma_g, \ldots$	−0.573146	−0.530494	−0.614410
$D_{3\sigma_g} = -0.452$	4	$1\sigma_g 3\sigma_g$	−0.457736	−0.452227	−0.516741

simply fully diagonalized by B. Thus all configurations in the MS are decoupled, and up to the 2-particle level, L_C assumes the form of an index-diagonal operator analogous to D in Eq. (2.5). This brute force determination of B worked unexpectedly well, and, as it is very convenient, it deserves further investigations.

The calculated energies (in h = hartree) of those four $^1\Sigma_g^+$ states of H_2 that have their dominant components in the MS are given in Table 2 for selected values of R. The $^1\Sigma_g^+$ states are characterized by their consecutive number and by their dominant configuration(s), and one should note that the states 3 and $4^1\Sigma_g^+$ do not necessarily correspond to the physical states with this count, mainly because the H_2^+ orbitals used as MOs in the calculations allow only for a poor first order description of these higher H_2 states.

In the first column of Table 2, the shift operator components are listed in the rows of the configurations directly affected by them. The shifts – which are chosen to be fairly continuous though not optimal – are applied in scheme a and in the approximate scheme b in the way as defined in Sect. 2.

As expected, scheme a always reproduces the full CI (FCI) results for the energies associated with non-shifted configurations, i.e. the main energies, whereas the intermediate energies are off by several 10 mh in positive direction. The values for scheme b are listed in order to demonstrate that the (uncorrected) shifts have only slight effects on the main energies; otherwise, the results from scheme b are not good enough to be of interest beyond this demonstration. Heully and Daudey [22] found the same weak dependence on the single shift parameter in their intermediate Hamiltonian scheme when applying it to the Be atom. This stability against specific choices for the shifts is very important for larger applications because the approximations required for large electronic systems will work only if the energies of interest are inherently nearly independent of the shifts.

For the schemes a and b, convergence was always reached in about 20 iterations for an accuracy of 10^{-6} h. The stability of the iteration procedure is particularly remarkable considering the fact that non-optimized orbitals were used.

5. Conclusions

It has been demonstrated that, using the intermediate Hamiltonian scheme presented in this work, the calculation of the potential energy curve of an excited molecular state in the framework of the Fock space effective Hamiltonian formalism is possible, in spite of the presence of intruder states. (The application to the H_2 molecule is meant to demonstrate only the viability of the method; naturally one would not normally calculate a 2-electron problem this way, but e.g. simply perform a full CI (configuration interaction) calculation.) Furthermore, the formalism, which results in shifted Bloch equations as working equations, provides a general way to intermediate Hamiltonians, while preserving the main features of the original effective Hamiltonian formalism: the particle number independence, the transparent access to connected diagram expansions, and the possibility of constructing (connected) *hermitian* effective Hamiltonians. Other advantages of the Fock space schemes proposed here are the flexibility in the choice of the shift terms and the applicability in both the complete and the incomplete model space cases. These results give rise to some optimism that the intruder problem plaguing the effective Hamiltonian approaches can be over-

come by generalizing the traditional approaches to intermediate Hamiltonian schemes. Since the techniques developed here are based on rather general principles, they can be expected to be helpful in calculating quasi-degenerate eigenvalues in any problem where this shift method is able to create a sufficiently large energy gap.

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