Theor Chim Acta (1995) 90: 421–439

Theoretica Chimica Acta

Orbital connections for perturbation-dependent basis sets

Jeppe Olsen[1], Keld L. Bak[2], Kenneth Ruud[3], Trygve Helgaker[3], Poul Jørgensen[4]

[1] Theoretical Chemistry, Chemical Centre, University of Lund, P.O. Box 124, S-22100 Lund, Sweden
[2] Department of Physical Chemistry, University of Copenhagen, DK-2100 København Ø, Denmark
[3] Department of Chemistry, University of Oslo, N-0315 Oslo, Norway
[4] Department of Chemistry, Aarhus University, D-8000 Aarhus, C, Denmark

Received May 31, 1994/Final version received September 12, 1994/Accepted September 26, 1994

Summary. The use of perturbation-dependent basis sets is analysed with emphasis on the connection between the basis sets at different values of the perturbation strength. A particular connection, the natural connection, that minimizes the change of the basis set orbitals is devised and the second quantization realization of this connection is introduced. It is shown that the natural connection is important for the efficient evaluation of molecular properties and for the physical interpretation of the terms entering the calculated properties. For example, in molecular Hessian calculations the natural connection reduces the size of the relaxation term, leading to faster convergence of the response equations. The physical separation of the terms also means that first-order non-adiabatic coupling matrix elements can be obtained in a very simple way from a molecular Hessian calculation.

Key words: Perturbation-dependent basis sets – Atomic orbitals – Molecular orbitals

1 Introduction

Molecular properties defined as energy derivatives can be calculated efficiently using physically motivated perturbation-dependent basis sets (PDBSs). With such sets, the basis set limit can be approached much faster than with basis sets that are independent of the perturbation. The two most common situations where PDBSs are encountered are in calculations of potential energy surfaces, where the atomic orbitals are clamped on the nuclei [1–3], and in calculations of magnetic properties using London atomic orbitals [also known as gauge invariant atomic orbitals (GIAOs) [4–8].

In PDBS calculations the basis set changes as the perturbation is turned on. This creates complications in the sense that it is not obvious what particular set of orthonormal orbitals should be used to represent the basis set at different values of perturbation strength x. In fact, at each x there exists an infinite number of orthonormal sets of orbitals. These sets are equivalent in the sense that they span the same orbital space, and they are all related through unitary transformations. However, in order to carry out the differentiation and calculate the properties, we must select exactly one such orthonormal set of orbitals for each value of x. In this way we establish a one-to-one correspondence between orthonormal orbitals ψ_m at different perturbation strengths. Such a one-to-one correspondence between orthonormal orbitals at different values of x is called an *orbital connection* [9].

An infinite number of orbital connections can be defined. The molecular properties are of course independent of the choice of connection. However, different connections shift contributions among the various terms entering the expression for the molecular property. This may create numerical problems and also clutter the physical interpretation of the individual terms. For example, in calculations of magnetic properties the choice of connection affects the paramagnetic and diamagnetic terms in such a way that the total property is unaffected [10]. The paramagnetic term is obtained by solving a set of linear equations to some prescribed numerical accuracy, and it is therefore most efficient to use connections where this term becomes as small as possible. All connections currently used have large paramagnetic contributions, and much effort is thus wasted by evaluating a large paramagnetic contribution that is nearly cancelled by a large diamagnetic term. Indeed, for large molecules the two contributions can become so large that the calculation of magnetizabilities becomes numerically unstable. Similarly, in calculations of the Cotton–Mouton effect, where the second derivative of the magnetizability with respect to an electric field is calculated, the standard choice of connection gives such large paramagnetic contributions that the calculated Cotton–Mouton constants become numerically unstable for large basis sets [10].

These problems may be avoided completely by a judicious choice of orbital connection based on physical principles. In the *natural connection* introduced in this paper, the above numerical problems are eliminated and it also becomes possible to give the diamagnetic and paramagnetic contributions a physical interpretation. For example, in the evaluation of magnetizabilities using the natural connection, the paramagnetic contribution includes only terms strictly related to the relaxation contribution, originating from the second-order energy contribution with the angular momentum operator as perturbation operator. The resulting paramagnetic term may therefore for example be used to calculate the paramagnetic contribution to the g rotational factor. This is not true for other connections. Our formulation allows, however, the identification of the true paramagnetic term also for a general connection.

We discuss in this paper the dependence of the creation and annihilation operators on x and describe the simplifications introduced by using the natural connection. We further examine the second-quantization Hamiltonian for PDBSs. In the limit of a complete basis, this Hamiltonian reduces to the one used in calculations with ordinary perturbation-independent basis sets. This Hamiltonian can therefore be used in time-dependent response function calculations, and frequency-dependent molecular properties can be determined using perturbation-dependent basis sets. Transition matrix elements can be obtained from the residues of the frequency-dependent response functions. The presented derivation allows the first rigorous derivation of frequency-dependent response functions and their residues using PDBSs.

In the subsequent paper we apply this development to determine the rotational strength in electronic circular dichrosim using London atomic orbitals. The rotational strength is obtained as the residue of the electric dipole–magnetic dipole linear response function, and is shown to be gauge-origin independent. Other examples where it is advantageous to use the natural connection is for the calculation of the non-adiabatic coupling matrix elements. These can actually be extracted in a very simple way from a molecular Hessian calculation when the natural connection is used. In a molecular Hessian calculation the size of the relaxation contribution is also reduced when the natural connection is used, thus improving the convegence of the response equations. Molecular Hessian can therefore be obtained more efficiently with the natural connection than with other connections. We return to these points in later publications.

In the next section we discuss different choices of orbital connections and introduce the natural orbital connection. In Sect. 3 we describe the creation and annihilation operator dependence on the PDBS and derive the operator realization of the orbital connection. In Sect. 4 we describe the simplifications that occur in the evaluation of overlap and matrix elements when the natural orbital connection is used. In the last section we discuss in more detail the implications of using the natural connection in molecular property calculations.

2 Orbital connections

We assume that the atomic basis functions depend on a vector of external parameters x. The vector x will in general contain several components, but for notational convenience the individual components of x are not referenced explicitly. For each value of x we have a set of atomic basis functions $\chi_\mu(x)$ and a basis of orthonormalized molecular orbitals (OMOs).

$$\psi_m(x) = \sum_\mu \chi_\mu(x) C_{\mu m}(x). \tag{1}$$

The Hamiltonian and wave functions can be expanded in these OMOs, and we may then proceed to optimize the wave function and the orbitals. Thus, the OMOs are in general not identical to the final optimized molecular orbitals at x. However, we do require that the OMOs become identical to the optimized molecular orbitals for the unperturbed system ($x = x_0$):

$$\phi_m(x_0) = \sum_\mu \chi_\mu(x_0)\, C^{(0)}_{\mu m}. \tag{2}$$

To accomplish this we introduce a set of unmodified molecular orbitals (UMOs)

$$\phi_m(x) = \sum_\mu \chi_\mu(x)\, C^{(0)}_{\mu m}. \qquad (2)$$

In general, the UMOs constitute a non-orthogonal basis set

$$S_{mn}(x) = \langle \phi_m(x) | \phi_n(x) \rangle \neq \delta_{mn}. \tag{4}$$

Provided the overlap matrix $\boldsymbol{S}$ is non-singular, the OMOs may be written as

$$\psi_m(x) = \sum_n \phi_n(x)\, T_{nm} \tag{5}$$

where the matrix $\boldsymbol{T}$ fulfils the requirement

$$\boldsymbol{T}^\dagger(x)\boldsymbol{S}(x)\boldsymbol{T}(x) = \boldsymbol{1} \tag{6}$$

By requiring that $\boldsymbol{T}(x_0) = \boldsymbol{1}$ we ensure that the OMOs reduce to the UMOs at x_0. In the following we will usually omit the argument x except for the unperturbed system $x = x_0$.

The above conditions are not sufficient to determine $\boldsymbol{T}$ uniquely. By rewriting Eq. (6) as $(\boldsymbol{S}^{1/2}\boldsymbol{T})^\dagger(\boldsymbol{S}^{1/2}\boldsymbol{T}) = \boldsymbol{1}$ we see that $\boldsymbol{S}^{1/2}\boldsymbol{T}$ must be a unitary matrix. Therefore, the number of undetermined parameters $\boldsymbol{T}$ fulfilling Eq. (6) equals the number of independent parameters in a unitary matrix. Any unitary matrix can be written as $\exp(-\kappa)$ where κ is an anti-Hermitian matrix. For real orbitals and real matrices, a unitary matrix has $n(n-1)/2$ independent parameters, and for complex orbitals and matrices there are n^2 undetermined parameters. Here n is the dimension of the basis set. In order to define the OMOs uniquely we must therefore supplement Eq. (6) with $n(n-1)/2$ and n^2 additional equations for real and complex orbitals, respectively. The choice of these equations thus establishes a one-to-one correspondence between the unperturbed molecular orbitals at x_0 and the OMOs at x. Such a one-to-one correspondence between sets of orbitals at different x is called an *orbital connection*, and the matrix $\boldsymbol{T}$ that determines this connection is referred to as the *connection matrix*.

From the above discussion we notice that if $\boldsymbol{T}$ fulfils Eq. (6), then for all other choices of $\boldsymbol{T}'$ fulfilling Eq. (6) can be generated as

$$\boldsymbol{T}' = \boldsymbol{T}\boldsymbol{U}, \tag{7}$$

where $\boldsymbol{U}$ is unitary. As expected, the specification of $\boldsymbol{U}$ requires $n(n-1)/2$ and n^2 independent parameters for real and complex matrices, which is identical to the number of equations that must be supplemented to Eq. (6) in order to specify $\boldsymbol{T}$ uniquely.

A simple way to establish the connection is to make some parts of $\boldsymbol{T}$ vanish. The Gram–Schmidt orthogonalization procedure corresponds to setting

$$\begin{aligned} T^{\mathrm{R}}_{mn} &= 0, \quad m > n, \\ T^{\mathrm{I}}_{mn} &= 0, \quad m \geqslant n, \end{aligned} \tag{8}$$

where we have written $\boldsymbol{T}$ as a sum of a real and an imaginary part $\boldsymbol{T} = \boldsymbol{T}^{\mathrm{R}} + \mathrm{i}\boldsymbol{T}^{\mathrm{I}}$. Although the Gram–Schmidt connection has been used in calculations [11], it lacks physical motivation. In particular, even in cases where $\chi_\mu(x_0)$ and $\chi_\mu(x)$ span the same space, the OMOs $\psi_m(x_0)$ and $\psi_m(x)$ will differ. This introduces unphysical terms when operators are expanded in the OMO basis. We return to this point later.

We now consider a group of connections where we augment Eq. (6) with the requirement that the functions $\psi_m(x)$ should be as similar as possible to some set of target functions $f_m(x)$. In analogy with Murrell [12] and Carlson and Keller [13] we therefore require that $\boldsymbol{T}$ minimizes the difference measure

$$\begin{aligned} \mathscr{D}(x) &= \sum_m \| f_m(x) - \psi_m(x) \|^2 \\ &= \sum_m \langle f_m(x) - \psi_m(x) | f_m(x) - \psi_m(x) \rangle \\ &= \sum_m [\langle f_m(x) | f_m(x) \rangle + 1] - \sum_m [\langle f_m(x) | \psi_m(x) \rangle + \langle \psi_m(x) | f_m(x) \rangle] \\ &= \sum_m [\langle f_m(x) | f_m(x) \rangle + 1] - \sum_m [(\boldsymbol{W}\boldsymbol{T})_{mm} + (\boldsymbol{W}\boldsymbol{T})^{\dagger}_{mm}] \end{aligned} \tag{9}$$

where we have introduced the matrix

$$W_{mn}(x) = \langle f_m(x) | \phi_n(x) \rangle. \tag{10}$$

We assume that $\boldsymbol{W}(x)$ is non-singular.

The first-order change in $\mathscr{D}(x)$ with respect to changes in $\boldsymbol{T}(x)$ can be written as

$$\delta\mathscr{D}(x) = -\sum_m [(\boldsymbol{W}\delta\boldsymbol{T})_{mm} + (\boldsymbol{W}\delta\boldsymbol{T})^{\dagger}_{mm}]. \tag{11}$$

Using an exponential parametrization of the unitary variation of $\boldsymbol{T}$, we obtain

$$\delta \boldsymbol{T} = \boldsymbol{T}\delta \boldsymbol{U} = -\boldsymbol{T}\kappa, \tag{12}$$

where κ is anti-Hermitian. Inserting this expression in Eq. (11) we obtain

$$\begin{aligned} \delta \mathscr{D}(x) &= \mathrm{Tr}[(\boldsymbol{WT})\boldsymbol{\kappa} - \kappa(\boldsymbol{WT})^{\dagger}] \\ &= \mathrm{Tr}[(\boldsymbol{WT}) - (\boldsymbol{WT})^{\dagger}]\boldsymbol{\kappa}. \end{aligned} \tag{13}$$

The matrix $\boldsymbol{\kappa}$ can be written as $\boldsymbol{\kappa} = \boldsymbol{\kappa}^{\mathrm{R}} + \mathrm{i}\boldsymbol{\kappa}^{\mathrm{I}}$, where $\boldsymbol{\kappa}^{\mathrm{R}}$ is a real antisymmetric matrix and $\boldsymbol{\kappa}^{\mathrm{I}}$ is a real symmetric matrix. Expansion of the variations in terms of the independent parameters of $\boldsymbol{\kappa}^{\mathrm{R}}$ and $\boldsymbol{\kappa}^{\mathrm{I}}$ gives

$$\begin{aligned} \delta \mathscr{D}(x) &= \mathrm{Tr}[\boldsymbol{WT} - (\boldsymbol{WT})^{\dagger}]\boldsymbol{\kappa}^{\mathrm{R}} + \mathrm{i}\,\mathrm{Tr}[\boldsymbol{WT} - (\boldsymbol{WT})^{\dagger}]\boldsymbol{\kappa}^{\mathrm{I}} \\ &= \sum_{m>n} [(\boldsymbol{WT})_{mn} - (\boldsymbol{WT})^{\dagger}_{mn} - (\boldsymbol{WT})_{nm} + (\boldsymbol{WT})^{\dagger}_{nm}]\,\kappa^{\mathrm{R}}_{nm} \\ &\quad + \mathrm{i}\sum_{m>n} [(\boldsymbol{WT})_{mn} - (\boldsymbol{WT})^{\dagger}_{mn} + (\boldsymbol{WT})_{nm} - (\boldsymbol{WT})^{\dagger}_{nm}]\,\kappa^{\mathrm{I}}_{nm} \\ &\quad + \sum_{m} [(\boldsymbol{WT})_{mm} - (\boldsymbol{WT})^{\dagger}_{mm}]\,\kappa^{\mathrm{I}}_{mm}. \end{aligned} \tag{14}$$

Requiring that the first-order change in $\mathscr{D}$ vanishes for any choice of $\boldsymbol{\kappa}^{\mathrm{R}}$ and $\boldsymbol{\kappa}^{\mathrm{I}}$, we obtain the Hermiticity relation

$$\boldsymbol{WT} = \boldsymbol{T}^{\dagger}\boldsymbol{W}^{\dagger}. \tag{15}$$

In order to obtain a closed expression for $\boldsymbol{T}$ we first write

$$\boldsymbol{T} = \boldsymbol{W}^{-1}\boldsymbol{M}. \tag{16}$$

Inserting this expression in Eq. (15), we find that $\boldsymbol{M}$ must be Hermitian:

$$\boldsymbol{M} = \boldsymbol{M}^{\dagger}. \tag{17}$$

The Hermitian matrix $\boldsymbol{M}$ may now be determined by inserting Eq. (16) into the orthogonality relation (6). We obtain

$$\boldsymbol{M}(\boldsymbol{W}^{\dagger})^{-1}\boldsymbol{S}\boldsymbol{W}^{-1}\boldsymbol{M} = \boldsymbol{M}(\boldsymbol{W}\boldsymbol{S}^{-1}\boldsymbol{W}^{\dagger})^{-1}\boldsymbol{M} = \mathbf{1}, \tag{18}$$

which has the solutions

$$\boldsymbol{M} = \pm(\boldsymbol{W}\boldsymbol{S}^{-1}\boldsymbol{W}^{\dagger})^{1/2} \tag{19}$$

and therefore

$$\boldsymbol{T} = \pm\boldsymbol{W}^{-1}(\boldsymbol{W}\boldsymbol{S}^{-1}\boldsymbol{W}^{\dagger})^{1/2}. \tag{20}$$

We have thus identified two choices of $\boldsymbol{T}$ that correspond to stationary points of $\mathscr{D}$. Since we require $\boldsymbol{T}(x_0) = \mathbf{1}$, we choose

$$\boldsymbol{T} = \boldsymbol{W}^{-1}(\boldsymbol{W}\boldsymbol{S}^{-1}\boldsymbol{W}^{\dagger})^{1/2}. \tag{21}$$

It can be shown that this choice corresponds to a minimum, while $\boldsymbol{T} = -\boldsymbol{W}^{-1}(\boldsymbol{W}\boldsymbol{S}^{-1}\boldsymbol{W}^{\dagger})^{1/2}$ maximizes $\mathscr{D}$.

By choosing different target functions, different connections can be generated. If we require the OMOs $\psi_m(x)$ to be as similar as possible to the UMOs $\phi_m(x)$ we set $f_m(x) = \phi_m(x)$. For this choice of $f_m(x)$, $\boldsymbol{W} = \boldsymbol{S}$, so Eq. (21) reduces to

$$\boldsymbol{T} = \boldsymbol{S}^{-1/2}. \tag{22}$$

This yields a symmetric connection matrix $\boldsymbol{T}$ and it is therefore called the symmetric connection. This connection can also be obtained directly from Eq. (6) by requiring $\boldsymbol{T}$ to be symmetric. However, the symmetric connections has – just like the Gram–Schmidt connection – no physical significance since OMOs are obtained using the unphysical UMOs as target functions. In particular, the OMOs $\psi_m(x_0)$ and $\psi_m(x)$ differ even when the basis sets span the same space. The symmetric connections has been used by a number of workers [14–16].

A more useful connection is obtained by requiring the basis functions $\psi_m(x)$ to be as similar as possible to the unperturbed molecular orbitals at x_0. The target functions are then given by $f_m(x) = \phi_m(x_0) = \psi_m(x_0)$ and the matrix $\boldsymbol{W}$ reads

$$W_{mn} = \langle \phi_m(x_0) | \phi_n(x) \rangle, \tag{23}$$

so the matrix we require to be Hermitian is

$$\Delta_{mn} = (\boldsymbol{W}\boldsymbol{T})_{mn} = \langle \psi_m(x_0) | \psi_n(x) \rangle, \tag{24}$$

This connection *minimizes the change in the basis functions* going from x_0 to x. In particular, we may show that if the two sets of basis functions $\chi_m(x_0)$ and $\chi_m(x)$ span the same space, we obtain $\psi_m(x) = \phi_m(x_0)$, so that the OMO functions do not change. This is a very desirable feature, which is only obtained with this connection, and we will therefore refer to this connection as the *natural connection.* To see this, we use the above assumption to expand the UMOs at x in terms of the UMOs at x_0:

$$\phi_m(x) = \sum_n \phi_n(x_0) L_{nm}. \tag{25}$$

Note that the matrix $\boldsymbol{L}(\boldsymbol{x})$ is not unitary since the UMOs at x are non-orthogonal. The matrices $\boldsymbol{W}$ and $\boldsymbol{S}$ can be written as

$$\begin{aligned} \boldsymbol{W}_{mn} &= \langle \phi_m(x_0) | \phi_n(x) \rangle = L_{mn}, \\ \boldsymbol{S}_{mn} &= \langle \phi_m(x) | \phi_n(x) \rangle = (\boldsymbol{L}^\dagger \boldsymbol{L})_{mn}, \end{aligned} \tag{26}$$

so the connection matrix Eq. (21) becomes $\boldsymbol{T} = \boldsymbol{L}^{-1}$, and the expansion in terms of UMOs is

$$\begin{aligned} \psi_m(x) &= \sum_n \phi_n(x) T_{nm} \\ &= \sum_p \phi_p(x_0)(\boldsymbol{L}\boldsymbol{L}^{-1})_{pm} \\ &= \phi_m(x_0) \end{aligned} \tag{27}$$

for a complete basis. For finite basis sets, the natural connection also has some unique features. Consider the projection of $\psi_m(x)$ onto the space spanned by $\psi_m(x_0)$:

$$\begin{aligned} \psi_m^{\mathrm{P}}(x) &= \sum_n \psi_n(x_0) \langle \psi_n(x_0) | \psi_m(x) \rangle \\ &= \sum_n \psi_n(x_0) \Delta_{nm}(x). \end{aligned} \tag{28}$$

Through first order in $\delta x = x - x_0$ we obtain

$$\psi_m^{\mathrm{P}}(x) = \psi_m(x_0) + \sum_n \psi_n(x_0) \left[\frac{\partial}{\partial x} \Delta_{nm}(x) \right] \delta x + O(\delta x^2). \tag{29}$$

Since the matrix Δ is Hermitian for all x, the matrix $(\partial/\partial x)\Delta$ is also Hermitian. But from the orthogonality relations $\langle\psi_n(x)|\psi_m(x)\rangle = \delta_{nm}$ it follows that $(\partial/\partial x)\Delta$ is anti-Hermitian. The matrix $(\partial/\partial x)\Delta$ must therefore vanish:

$$\left[\frac{\partial}{\partial x}\Delta_{nm}(x)\right] = \left\langle\psi_m(x_0)\left|\frac{\partial}{\partial x}\psi_n(x)\right.\right\rangle = 0 \tag{30}$$

and we see that to first order in the perturbation the projected differentiated OMOs are identical to the unperturbed orbitals

$$\psi_m^{\mathrm{P}}(x) = \psi_m(x_0) + O(\delta x^2). \tag{31}$$

The natural connection thus ensures that the OMOs for a general x are as similar as possible to the corresponding unperturbed orbitals. It will be shown in Sect. 4 that this ensures a physically reasonable expansion of the operators used to calculate derivatives of molecular energies and properties. In order to use the natural connection in the calculation of derivatives of wave functions and properties, it is necessary to obtain derivatives of $\boldsymbol{T}$. The first and second derivatives of $\boldsymbol{T}$ are given in Appendix A.

3 Second-quantization representation of connections

For our discussion of second-quantization operators [17–19] it is convenient to introduce a complete orthonormal orbital space, consisting of the finite set of OMOs and an associated orthogonal complement set of orbitals. In the following we will refer to the orbitals spanning the complement as the orthogonal complement orbitals (OCOs). We distinguish these orbitals by using indices m and n for the OMOs and u and v for the OCOs. Indices p and q are used for unspecified orbitals belonging to either the OMO space or its complement. An arbitrary orbital may now be expanded exactly in these orbitals:

$$\phi = \sum_p c_p\psi_p(x) = \sum_m c_m\psi_m(x) + \sum_u c_u\psi_u(x). \tag{32}$$

In particular, complete orthonormal basis sets at different x are related by a unitary transformation

$$\psi_p(x) = \sum_q \psi_q(x_0)U_{qp}(x), \tag{33}$$

where

$$\boldsymbol{U}^\dagger(x)\boldsymbol{U}(x) = \boldsymbol{U}(x)\boldsymbol{U}^\dagger(x) = \mathbf{1}. \tag{34}$$

An explicit parametrization of the unitary matrix $\boldsymbol{U}(x)$ is given by

$$\boldsymbol{U}(x) = \exp[-\boldsymbol{b}(x)], \tag{35}$$

where $\boldsymbol{b}(x)$ is an anti-Hermitian matrix

$$\boldsymbol{b}^\dagger(x) = -\boldsymbol{b}(x). \tag{36}$$

From Eq. (36) we see that there are P^2 independent parameters in $\boldsymbol{b}(x)$, where P is the dimension of the matrix. We may for example choose the complex numbers below the diagonal and the imaginary numbers on the diagonal as the free parameters. The remaining elements are obtained from Eq. (36).

Analogously, we may now expand the creation and annihilation operators at x exactly in terms of the operators at x_0:

$$a_p^\dagger(x) = \sum_q a_q^\dagger(x_0)\, U_{qp}(x), \tag{37}$$

$$a_p(x) = \sum_q a_q(x_0)\, U_{qp}^*(x). \tag{38}$$

An operator representation of the unitary transformation of the creation and annihilation operators can be written in terms of the unitary operator $\hat{U}(x)$ (see for example [20]):

$$a_p^\dagger(x) = \hat{U}(x) a_p^\dagger(x_0) \hat{U}^\dagger(x), \tag{39}$$

$$a_p(x) = \hat{U}(x) a_p(x_0) \hat{U}^\dagger(x), \tag{40}$$

where

$$\hat{U}(x) = \exp[-\hat{b}(x)], \tag{41}$$

$$\hat{b}(x) = \sum_{pq} b_{pq}(x) a_p^\dagger(x_0) a_q(x_0) \tag{42}$$

and the parameters $b_{pq}(x)$ are the elements of the anti-Hermitian matrix $\boldsymbol{b}(x)$. This unitary operator may then also be used to carry out unitary transformations of occupation number (ON) vectors in Fock space:

$$|N(x)\rangle = \hat{U}(x)|N(x_0)\rangle. \tag{43}$$

The purpose of this section is to study the form of the anti-Hermitian operator $\hat{b}(x)$ corresponding to the unitary transformation of OMOs at different values of the perturbation strength x. We will not derive an explicit form for $\hat{b}(x)$, rather we are interested in the expansion of the operator around x_0:

$$\hat{b}(x) = \hat{b}^{(0)} + \hat{b}^{(1)}\delta x + \tfrac{1}{2}\hat{b}^{(2)}\delta x^2 + \cdots, \tag{44}$$

where

$$\hat{b}^{(k)} = \sum_{pq} b_{pq}^{(k)} a_p^\dagger(x_0) a_q(x_0). \tag{45}$$

Once the detailed form of this expansion is known, we may calculate the unitary operator $\hat{U}(x)$ to a given order and carry out the associated transformations of operators and states given by Eqs. (39), (40), and (43).

Differentiating Eq. (35) and identifying terms to the same order in x, we obtain to second order:

$$\boldsymbol{b}^{(0)} = \boldsymbol{0}, \tag{46}$$

$$\boldsymbol{b}^{(1)} = -\boldsymbol{U}^{(1)}, \tag{47}$$

$$\boldsymbol{b}^{(2)} = -\boldsymbol{U}^{(2)} + \boldsymbol{U}^{(1)}\boldsymbol{U}^{(1)}. \tag{48}$$

We have here used the fact that for the unperturbed system

$$\boldsymbol{U}(x_0) = \boldsymbol{U}^{(0)} = \boldsymbol{1} \tag{49}$$

to simplify the expressions. Thus, the perturbed operator given by Eq. (44) may be calculated from the derivatives of the unitary matrix $\boldsymbol{U}(x)$.

Differentiating the unitary condition given by Eq. (34), we find that the Hermitian part of the nth derivative of the unitary matrix may be calculated from lower-order derivatives. In particular, for first and second derivatives we obtain

$$\boldsymbol{U}_{\mathrm{H}}^{(1)} = \frac{\boldsymbol{U}^{(1)} + \boldsymbol{U}^{(1)\dagger}}{2} = \mathbf{0}, \tag{50}$$

$$\boldsymbol{U}_{\mathrm{H}}^{(2)} = \frac{\boldsymbol{U}^{(2)} + \boldsymbol{U}^{(2)\dagger}}{2} = \boldsymbol{U}^{(1)}\boldsymbol{U}^{(1)}, \tag{51}$$

where the subscript H indicates the Hermitian part of $\boldsymbol{U}$. The first derivatives of unitary matrices are therefore anti-Hermitian. Using Eq. (51), we may now write Eq. (48) in the following two equivalent ways:

$$\begin{aligned} \boldsymbol{b}^{(2)} &= -\boldsymbol{U}^{(2)} + \boldsymbol{U}^{(1)}\boldsymbol{U}^{(1)} \\ &= -\tfrac{1}{2}[\boldsymbol{U}^{(2)} - \boldsymbol{U}^{(2)\dagger}] = \boldsymbol{U}_{\mathrm{A}}^{(2)}, \end{aligned} \tag{52}$$

where the subscript A indicates the anti-Hermitian part of $\boldsymbol{U}$. The last expression displays more clearly the anti-Hermitian nature of the matrix $\boldsymbol{b}^{(2)}$. Of course, by differentiating the anti-Hermitian condition given by Eq. (36) we see that $\boldsymbol{b}^{(n)}$ is anti-Hermitian to all orders.

Before considering the detailed form of the first and second derivatives of the operator $\hat{b}(x)$, we note that the matrix $\boldsymbol{b}(x)$ may be partitioned in blocks corresponding to the OMOs and OCOs:

$$\boldsymbol{b}(x) = \begin{bmatrix} \boldsymbol{F}(x) & -\boldsymbol{G}^{\dagger}(x) \\ \boldsymbol{G}(x) & \boldsymbol{K}(x) \end{bmatrix}. \tag{53}$$

To first order in Eq. (35), $\boldsymbol{F}(x)$ describes transformations among the OMOs, $\boldsymbol{K}(x)$ describes transformations among the OCOs, and $\boldsymbol{G}(x)$ corresponds to transformations mixing OMOs with the OCOs. Since we are not concerned with internal transformations among the OCOs, we may simplify our expressions by requiring

$$\boldsymbol{K}(x) \equiv \mathbf{0} \tag{54}$$

for all values of x. This choice does not in any way restrict our freedom in describing the OMOs, as can be shown by group theoretical arguments.

Further simplifications arise for the natural connection. The unitary matrix $\boldsymbol{U}(x)$ may be written in the following blocked form:

$$\boldsymbol{U}(x) = \begin{bmatrix} \boldsymbol{\Delta}(x) & \boldsymbol{\Lambda}(x) \\ \boldsymbol{\Phi}(x) & \boldsymbol{\Omega}(x) \end{bmatrix}, \tag{55}$$

where

$$\Delta_{mn}(x) = \langle \psi_m(x_0) | \psi_n(x) \rangle, \tag{56}$$

$$\Phi_{un}(x) = \langle \psi_u(x_0) | \psi_n(x) \rangle, \tag{57}$$

$$\Lambda_{mv}(x) = \langle \psi_m(x_0) | \psi_v(x) \rangle, \tag{58}$$

$$\Omega_{uv}(x) = \langle \psi_u(x_0) | \psi_v(x) \rangle. \tag{59}$$

For natural connections $\boldsymbol{\Delta}(x)$ is Hermitian and we may also require $\boldsymbol{\Omega}(x)$ to be Hermitian:

$${}^{\mathrm{nc}}\boldsymbol{\Delta}^{\dagger} = {}^{\mathrm{nc}}\boldsymbol{\Delta}, \tag{60}$$

$${}^{\mathrm{nc}}\boldsymbol{\Omega}^{\dagger} = {}^{\mathrm{nc}}\boldsymbol{\Omega}, \tag{61}$$

where the upper left superscript nc indicates the natural connection. As discussed in Appendix B, a unitary matrix with Hermitian diagonal blocks may be written as the exponential of an anti-Hermitian matrix with zero diagonal blocks. Thus, for the natural connection we may write

$$^{\mathrm{nc}}\boldsymbol{b}(x) = \begin{bmatrix} \mathbf{0} & -\boldsymbol{G}^{\dagger}(x) \\ \boldsymbol{G}(x) & \mathbf{0} \end{bmatrix}. \tag{62}$$

To summarize, the anti-Hermitian matrix $\boldsymbol{b}(x)$ may be written in the form of Eq. (53) with $\boldsymbol{K}(x)$ equal to zero. For the natural connection $\boldsymbol{F}(x)$ vanishes [Eq. (62)].

We now return to the problem of evaluating the derivatives of the $\hat{b}(x)$ in Eq. (42). The first derivative is given by

$$\hat{b}^{(1)}(x) = \sum_{mn} b_{mn}^{(1)} a_m^{\dagger}(x_0) a_n(x_0) + \sum_{un} b_{un}^{(1)} a_u^{\dagger}(x_0) a_n(x_0) + \sum_{nu} b_{nu}^{(1)} a_n^{\dagger}(x_0) a_u(x_0), \tag{63}$$

where we have used the fact that $\boldsymbol{K}(x)$ vanishes to all orders to simplify the summation:

$$b_{uv}^{(1)} \equiv 0. \tag{64}$$

From Eq. (47) we obtain

$$\hat{b}^{(1)} = -\sum_{mn} U_{mn}^{(1)} a_m^{\dagger}(x_0) a_n(x_0) - \sum_{un} U_{un}^{(1)} a_u^{\dagger}(x_0) a_n(x_0) + \sum_{un} b_{un}^{(1)*} a_n^{\dagger}(x_0) a_u(x_0), \tag{65}$$

where we have also used the fact that $\boldsymbol{U}^{(1)}$ is anti-Hermitian. We now expand the derivatives of the OMO creation operators in the unperturbed OMO and OCO creation operators:

$$a_m^{\dagger(k)} = \sum_p a_p^{\dagger}(x_0) U_{pm}^{(k)}. \tag{66}$$

It is convenient to decompose these derivatives in components spanned by the OMOs and by the OCOs:

$$a_m^{\dagger(k)} = a_{m\parallel}^{\dagger(k)} + a_{m\perp}^{\dagger(k)} \tag{67}$$

where

$$a_{m\parallel}^{\dagger(k)} = \sum_n a_n^{\dagger}(x_0) U_{nm}^{(k)}, \tag{68}$$

$$a_{m\perp}^{\dagger(k)} = \sum_n a_u^{\dagger}(x_0) U_{um}^{(k)}. \tag{69}$$

The annihilation operators are partitioned in the same manner. We may now write Eq. (65) as

$$\hat{b}^{(1)} = -\sum_m a_{m\parallel}^{\dagger(\dagger)} a_m^{(0)} - \sum_m a_{m\perp}^{(1)\dagger} a_m^{(0)} + \sum_m a_m^{(0)\dagger} a_{m\perp}^{(1)}. \tag{70}$$

We see that the first derivative of the anti-Hermitian $\hat{b}$ operator may be written as sums over undifferentiated and differentiated OMO creation and annihilation operators.

Equation (70) is quite general and we have made no assumptions about the connection. In the natural connection, the OMO–OMO block of $\boldsymbol{b}(x)$ vanishes and we have the following simplification:

$$^{\mathrm{nc}}U_{mn}^{(1)} = 0 \;\Rightarrow\; ^{\mathrm{nc}}a_{m\parallel}^{(1)\dagger} = 0 \tag{71}$$

and hence

$$ {}^{\mathrm{nc}}\hat{b}^{(1)} = -\sum_{m} a^{(1)\dagger}_{m\perp} a^{(0)}_{m} + \sum_{m} a^{(0)\dagger}_{m} a^{(1)}_{m\perp} . \tag{72} $$

Thus, in the natural connection the only surviving terms are those mixing OMO orbitals with their projected derivatives in the orthogonal complement.

We now turn to the second derivatives, which may be written in the form

$$ \hat{b}^{(2)} = \sum_{mn} b^{(2)}_{mn} a^{\dagger}_{m}(x_0)\, a_{n}(x_0) + \sum_{un} b^{(2)}_{un} a^{\dagger}_{u}(x_0)\, a_{n}(x_0) + \sum_{nu} b^{(2)}_{nu} a^{\dagger}_{n}(x_0)\, a_{u}(x_0). \tag{73} $$

We use the following identification:

$$ \begin{aligned} b^{(2)}_{mn} &= -\tfrac{1}{2}\left[U^{(2)}_{mn} - U^{(2)*}_{nm}\right], \\ b^{(2)}_{un} &= -U^{(2)}_{un} + \sum_{p} U^{(1)}_{up} U^{(1)}_{pn} \end{aligned} \tag{74} $$

$$ = -U^{(2)}_{un} + \sum_{m} U^{(1)}_{um} U^{(1)}_{mn} \tag{75} $$

$$ b^{(2)}_{nu} = -b^{(2)*}_{un} = U^{(2)*}_{un} - \sum_{m} U^{(1)}_{mu} U^{(1)}_{nm}. \tag{76} $$

Here Eq. (74) follows directly from Eq. (52), while Eq. (75) follows from Eq. (52) and from the relationship

$$ U^{(1)}_{uv} = -b^{(1)}_{uv} \equiv 0 \tag{77} $$

and in Eq. (76) we have used the fact that U^{1} is anti-Hermitian [see Eq. (47)]. Inserting Eqs. (74)–(76) into Eq. (73) we obtain

$$ \begin{aligned} \hat{b}^{(2)} = &-\frac{1}{2}\sum_{mn} U^{(2)}_{mn} a^{\dagger}_{m}(x_0)\, a_{n}(x_0) + \frac{1}{2}\sum_{mn} U^{(2)*}_{nm} a^{\dagger}_{m}(x_0)\, a_{n}(x_0) \\ &- \sum_{un} U^{(2)}_{un} a^{\dagger}_{u}(x_0)\, a_{n}(x_0) + \sum_{un} U^{(2)*}_{un} a^{\dagger}_{n}(x_0)\, a_{u}(x_0) \\ &+ \sum_{umn} U^{(1)}_{um} U^{(1)}_{mn} a^{\dagger}_{u}(x_0)\, a_{n}(x_0) - \sum_{umn} U^{(1)}_{mu} U^{(1)}_{mn} a^{\dagger}_{n}(x_0)\, a_{u}(x_0) \end{aligned} \tag{78} $$

We now introduce the derivatives given by Eqs. (68) and (69) and obtain

$$ \begin{aligned} \hat{b}^{(2)} = &-\frac{1}{2}\sum_{m} a^{(2)\dagger}_{m\parallel} a^{(0)}_{m} + \frac{1}{2}\sum_{m} a^{(0)\dagger}_{m} a^{(2)}_{m\perp} \\ &- \sum_{m} a^{(2)\dagger}_{m\perp} a^{(0)}_{m} + \sum_{m} a^{(0)\dagger}_{m} a^{(2)}_{m\perp} \\ &- \sum_{m} a^{(1)\dagger}_{m\perp} a^{(1)}_{m\perp} + \sum_{m} a^{(1)\dagger}_{m\parallel} a^{(1)}_{m\perp} . \end{aligned} \tag{79} $$

Again, the operator is expressed entirely in terms of OMOs and their derivatives. For the natural connection, many of the terms vanish because of Eq. (71), and we obtain the simple expression

$$ {}^{\mathrm{nc}}\hat{b}^{(2)} = -\sum_{m} a^{(2)\dagger}_{m\perp} a^{(0)}_{m} + \sum_{m} a^{(0)\dagger}_{m} a^{(2)}_{m\perp} \tag{80} $$

which may be compared with the analogous expression for the first derivative given by Eq. (72).

In the expressions developed for the derivatives of $\hat{b}(x)$ there is no explicit reference to the OCOs. Indeed, no such information is ever needed, since in actual calculations the $\hat{b}(x)$ operator is always sandwiched between bra and ket states and we only need to be able to determine the anticommutators between the creation and annihilation operators entering $\hat{b}(x)$. For example, in the natural connection the only new non-vanishing anticommutators that arise to first order in the perturbation are those between the projected creation operators $a^{(1)\dagger}_{m\perp}$ and the projected annihilation $a^{(1)}_{m\perp}$ operators. These are easily obtained as

$$[a^{(1)}_{m\perp}, a^{(1)}_{n\perp}]_+ = \langle \psi^{(1)}_{m\perp} | \psi^{(1)}_{n\perp} \rangle, \tag{81}$$

where we have introduced the projection of the differentiated OMOs onto the orthogonal complement:

$$\psi^{(1)}_{m\perp} = \psi^{(1)}_{m} - \sum_{n} \psi_n(x_0)\, U^{(1)}_{nm}. \tag{82}$$

Inserting this expression into Eq. (81) we obtain

$$[a^{(1)}_{m\perp}, a^{(1)}_{n\perp}]_+ = \langle \psi^{(1)}_{m} | \psi^{(1)}_{n} \rangle - [\Delta^{(1)\dagger} \Delta^{(1)}]_{mn}, \tag{83}$$

which for the natural connection simplifies to

$$[{}^{\mathrm{nc}}a^{(1)}_{m\perp}, {}^{\mathrm{nc}}a^{(1)}_{n\perp}]_+ = \langle \psi^{(1)}_{m} | \psi^{(1)}_{n} \rangle \tag{84}$$

since the first derivative OMOs have no projection in the unperturbed OMO space.

4 Overlaps and matrix elements

In this section we first examine overlaps between ON vectors at different values of x and show how the connection operator $\hat{U}$ can be used to obtain the results in a straightforward manner. Next we analyze the perturbation dependence of second-quantization operators and expectation values. Consider the overlap between two ON vectors at the same x:

$$\begin{aligned} \langle N(x) | M(x) \rangle &= \langle N(x_0) | \hat{U}^\dagger \hat{U} | M(x_0) \} \\ &= \langle N(x_0) | M(x_0) \rangle. \end{aligned} \tag{85}$$

Hence, the perturbation dependence of the matrix element disappears. Consider now a matrix element $\langle N(x_0) | M(x) \rangle$ where only $|M(x)\rangle$ depends on x. In the natural connection we obtain

$$\begin{aligned} \langle N(x_0) | M(x) \rangle &= \langle N(x_0) | \hat{U} | M(x_0) \rangle \\ &= \langle N(x_0) | M(x_0) \rangle - \langle N(x_0) | \hat{b}^{(1)} | M(x_0) \rangle \delta x \\ &\quad - \tfrac{1}{2} [\langle N(x_0) | \hat{b}^{(2)} | M(x_0) \rangle \\ &\quad - \langle N(x_0) | \hat{b}^{(1)} \hat{b}^{(1)} | M(x_0) \rangle] \delta x^2 + O(\delta x^3) \\ &= \langle N(x_0) | M(x_0) \rangle \\ &\quad - \frac{1}{2} \sum_{mn} \langle N(x_0) | a^\dagger_m(x_0) a^{(1)}_{m\perp} a^{(1)\dagger}_{n\perp} a_n(x_0) | M(x_0) \rangle \delta x^2 + O(\delta x^3) \\ &= \langle N(x_0) | M(x_0) \rangle \\ &\quad - \frac{1}{2} \sum_{mn} \langle N(x_0) | a^\dagger_m(x_0) a_n(x_0) | M(x_0) \rangle [a^{(1)}_{m\perp}, a^{(1)\dagger}_{n\perp}]_+ \delta x^2 + O(\delta x^3). \end{aligned} \tag{86}$$

To obtain Eq. (86) we have used the fact that the expectation values of $\hat{b}^{(1)}$ and $\hat{b}^{(2)}$ given in Eqs. (72) and (80) vanish. For the natural connection, the first derivatives vanish,

$$\frac{\partial}{\partial x}\langle N(x_0)|M(x)\rangle\Big|_{x=x_0} = 0, \tag{87}$$

and the second derivatives are

$$\frac{\partial^2}{\partial x^2}\langle N(x_0)|M(x)\rangle|_{x=x_0} = -\sum_{mn}\langle N(x_0)|a_m^\dagger(x_0)a_n(x_0)|M(x_0)\rangle\left\langle\frac{\partial\psi_m}{\partial x}\middle|\frac{\partial\psi_n}{\partial x}\right\rangle. \tag{88}$$

Equations (87) and (88) can be used to obtain the contribution from the perturbation dependence of the creation and annihilation operators to non-adiabatic coupling matrix elements [21]. We note that this contribution vanishes for first-order non-adiabatic coupling matrix elements in the natural connection. Matrix elements $\langle \partial N(x)/\partial x\,|\,\partial M(x)/\partial x\rangle$ can be similarly be obtained as

$$\begin{aligned}\left\langle\frac{\partial N(x)}{\partial x}\middle|\frac{\partial M(x)}{\partial x}\right\rangle &= -2\langle N(x_0)|\hat{b}^{(1)}\hat{b}^{(1)}|M(x_0)\rangle \\ &= 2\sum_{mn}\langle N(x_0)|a_m^\dagger(x_0)a_n(x_0)|M(x_0)\rangle\left\langle\frac{\partial\psi_m}{\partial x}\middle|\frac{\partial\psi_n}{\partial x}\right\rangle,\end{aligned} \tag{89}$$

Such matrix elements are for example needed for the evaluation of vibrational circular dichroism (VCD) tensors [22]. If a general connection had been used, the above expressions would become significantly more complicated.

Equation (87) reflects an important property of the natural connection: the projections of the ON vectors in the space spanned by the unperturbed orbitals do not change to first order in the perturbation. Since our molecular orbital basis is finite, we cannot hope to make the ON vectors independent of the perturbation. However, we do have some freedom in choosing our basis set at x, and in the natural connection we use this freedom to make the changes in the ON vectors as small as possible as seen from Eq. (87).

We next examine operators and expectation values for PDBSs, and their dependence upon connections. For simplicity we will restrict our attention to one-body operators. The generalization to two-body operators is straightforward. The first-quantization one-body operator $h^c(x)$ has the representations $\hat{h}(x_0)$ and $\hat{h}(x)$ at x and x_0:

$$\begin{aligned}\hat{h}(x_0) &= \sum_{mn} h_{mn}(x_0)a_m^\dagger(x_0)a_n(x_0),\\ \hat{h}(x) &= \sum_{mn} h_{mn}(x)a_m^\dagger(x)a_n(x).\end{aligned} \tag{90}$$

Here $h_{mn}(x)$ are the integrals over the OMOs $\psi_m(x)$:

$$h_{mn}(x) = \int \psi_m^*(x)h(x)\psi_n(x)\,\mathrm{d}\tau \tag{91}$$

and $h_{mn}(x_0)$ are the integrals over the OMOs $\psi_m(x_0)$.

The operator $\hat{h}(x)$ depends upon x through the OMOs $\psi_m(x)$, through the explicit dependence of the operator $h^c(x)$, and through the creation and annihilation operators $a_m^\dagger(x)$ and $a_n(x)$. In the limit of a complete basis, the x dependence of the OMOs $\psi_m(x)$ must cancel the x dependence of the creation and annihilation operators $a_m^\dagger(x)$ and $a_n(x)$, leaving only the explicit x dependence of the first-quantization operator $h^c(x)$. This can be demonstrated as follows. For a complete basis we may use the unitary expansions given by Eq. (33) for the orbitals and Eqs. (37) and (38) for the creation and annihilation operators. Inserting these expansions in Eq. (90), we obtain

$$\begin{aligned}\hat{h}(x) &= \sum_{m,n}\left[\sum_{m'n'} U_{m'm}^{*} \int \psi_{m'}^{*}(x_0)h(x)\psi_{n'}(x_0)\,\mathrm{d}\tau\, U_{n'n}\right] \sum_{m''n''} a_{m''}^{\dagger} U_{m''m} a_{n''} U_{n''n}^{*} \\ &= \sum_{m',m''n'n''} [UU^\dagger]_{m''m'} [UU^\dagger]_{n''n'} \int \psi_m^{*}(x_0)h(x)\psi_n(x_0)\,\mathrm{d}\tau\, a_{m''}^{\dagger} a_{n''} \\ &= \sum_{m',m''n'n''} \delta_{m''m'}\delta_{n''n'} \int \psi_m^{*}(x_0)h(x)\psi_n(x_0)\,\mathrm{d}\tau\, a_{m''}^{\dagger} a_{n''} \end{aligned} \tag{92}$$

which gives us the required result

$$\hat{h}(x) = \sum_{m,n} \int \psi_m(x_0)h(x)\psi_n^{*}(x_0)\,\mathrm{d}\tau\, a_m^\dagger(x_0)a_n(x_0). \tag{93}$$

Comparing this expression with Eq. (90), we see that for a complete basis set at the perturbation dependence of the OMOs and the creation and annihilation operators cancel out.

In calculations of derivatives of the electronic energy or/and electronic properties, the operator and the wave functions all refer to identical values of x so the involved matrix elements are

$$\begin{aligned}\langle N(x)|\hat{h}(x)|M(x)\rangle &= \sum_{m,n} h_{mn}(x)\langle N(x)|a_m^\dagger(x)a_n(x)|M(x)\rangle \\ &= \sum_{mn} h_{mn}(x)\langle N(x_0)|\hat{U}^\dagger(x)\hat{U}(x)a_m^\dagger(x_0)\hat{U}^\dagger(x) \\ &\quad\times \hat{U}(x)a_n(x_0)\hat{U}^\dagger(x)\hat{U}(x)|M(x_0)\rangle. \end{aligned} \tag{94}$$

From this we conclude that the transition expectation value may be calculated as

$$\langle N(x)|\hat{h}(x)|M(x)\rangle = \sum_{m,n} h_{mn}(x)\langle N(x_0)|a_m^\dagger(x_0)a_n(x_0)|M(x_0)\rangle. \tag{95}$$

For the purpose of calculating adiabatic expectation values and transition expectation values, we may thus neglect the perturbation dependence of the creation and annihilation operators as well as the ON vectors. This is the case, for example, in the calculation of molecular gradients and Hessians, shielding constants, and magnetizabilities. For such adiabatic properties we may consider

$$\hat{U}^\dagger\hat{h}(x)\hat{U} = \sum_{mn} h_{mn}(x)a_m^\dagger(x_0)a_n(x_0) \tag{96}$$

an effective operator to be used with the ON vectors $|M(x_0)\rangle$. It should be noted, however, that the operator $\hat{U}^\dagger\hat{h}(x)\hat{U}$ does not have any physical significance except when sandwiched between unperturbed ON vectors. For example, although the operator $\hat{h}(x)$ is independent of the choice of connection, the transformed operator $\hat{U}^\dagger\hat{h}(x)\hat{U}$ is not connection-independent. We will return to this aspect in the next section.

In derivative theory, the operators are expanded in orders of δx. The expansion of the full operator $\hat{h}(x)$ and the operator with perturbation dependence only through the integrals, $\hat{U}^\dagger \hat{h}(x)\hat{U}$, can be written as

$$\begin{aligned}\hat{h}(x) &= \hat{h}(x_0) + \hat{h}^{[1]}\delta x + \tfrac{1}{2}\hat{h}^{[2]}\,\delta x\,\delta x,\\ \hat{U}^\dagger \hat{h}(x)\hat{U} &= \hat{h}(x_0) + \hat{h}^{(1)}\delta x + \tfrac{1}{2}\hat{h}^{(2)}\delta x\delta x.\end{aligned} \tag{97}$$

The operators $\hat{h}^{[n]}$ are independent of connection and will in the limit of a complete basis become

$$\hat{h}^{[n]} = \sum_{m,n} \int \psi_m^*(x_0)\frac{\partial^n h(x)}{\partial x^n}\psi_n(x_0)\,\mathrm{d}\tau\; a_m^\dagger(x_0)a_n(x_0). \tag{98}$$

The operators $\hat{h}(n)$ depend upon the actual connection and will in general not be given by the right-hand side of Eq. (98) in the complete basis set limit.

5 Response properties

To illustrate how connection-dependent terms occur in derivatives of energies and how the true static and response terms can be obtained, we will consider time-independent response theory for variational wave functions. We assume that for $x = x_0$ a proper optimized wave function $|O(x_0)\rangle$ is given, and write the wave function for a general value of x as

$$|O(x)\rangle = \exp[-\hat{b}(x)]\exp[-\mathcal{O}(x)]|O(x_0)\rangle. \tag{99}$$

The operator $\exp[-\hat{b}(x)]$ changes the OMOs, and the operator $\exp[-\mathcal{O}(x)]$ changes the electronic parameters describing the wave function. For an SCF wave function $\mathcal{O}(x)$ is an anti-Hermitian one-electron operator defined in terms of the creation and annihilation operators at x_0, allowing optimization (relaxation) of the molecular orbitals. For a CI wave function $\mathcal{O}(x)$ is an anti-Hermitian operator allowing relaxation of the CI coefficients. Wave functions where orbitals and CI coefficients both relax requires a double exponential formalism which is a trivial extension of the following.

The parameters of $\exp[-\mathcal{O}(x)]$ are expanded in powers of δx and are determined by requiring that the following energy is stationary:

$$\begin{aligned}E(x) &= \langle \mathcal{O}(x)|\hat{H}(x)|O(x)\rangle\\ &= \langle O(x_0)|\exp[\mathcal{O}(x)]\exp[\hat{b}(x)]H(x)[-\hat{b}(x)]\\ &\quad\times\exp[-\mathcal{O}(x)]|O(x_0)\rangle,\end{aligned} \tag{100}$$

where $\hat{H}(x)$ is the perturbation-dependent Hamiltonian. It is convenient to consider $\exp[\hat{b}(x)]\hat{H}(x)[-\hat{b}(x)]$ to be an effective Hamiltonian, since the creation and annihilation operators then become perturbation-independent. This corresponds to moving a part of the wave function response into the Hamiltonian operator. We will soon return to the consequences of this. Expanding $\exp[\hat{b}(x)]\hat{H}(x)[-\hat{b}(x)]$ according to Eq. (97) gives through second order in δx

$$\begin{aligned}E(x) = \langle O(x_0)|\hat{H}|O(x_0)\rangle&\\ + \langle O(x_0)|\hat{H}^{(1)}|O(x_0)\rangle\delta x&\\ + (\langle O(x_0)|\hat{H}^{(2)}|O(x_0)\rangle&\\ + \langle O(x_0)|[\mathcal{O}^{(1)},\hat{H}^{(1)}]|O(x_0)\rangle&\\ + \tfrac{1}{2}\langle O(x_0)|[\mathcal{O}^{(1)}[\mathcal{O}^{(1)},\hat{H}]]|O(x_0)\rangle)\delta x\delta x.&\end{aligned} \tag{101}$$

In the above expansion we have used the fact that $|O(x_0)\rangle$ is optimized with respect to variations of $\mathcal{O}$ and assumed the Brillouin conditions $\langle O(x_0)| [a_m^\dagger(x_0)a_n(x_0), \hat{H}]|O(x_0)\rangle = \mathbf{0}$ to simplify the terms. The first-order terms do not include any contribution from wave function changes. The second-order terms contain the static term $\langle O(x_0)|\hat{H}^{(2)}|O(x_0)\rangle$ and a response term arising from the first-order correction to the wave function.

The above separation of static and response terms is with respect to the effective Hamiltonian $\exp[\hat{b}(x)]\,\hat{H}(x)[-\hat{b}(x)]$. As discussed above, this operator contains a part of the wave function response and does not correspond to any physical perturbation. This rearrangement does not change the total second-order energy, but for cases where the static and the response terms each have a physical interpretation it is very useful to have a formalism where the true static and dynamic terms can be correctly obtained. This is achieved by using the physically correct Hamiltonian $\hat{H}(x)$. Repeating the above derivation for this partitioning of wave function and Hamiltonian one obtains the true static contribution to a second-order energy as $\langle O(x_0)|\hat{H}^{[2]}|O(x_0)\rangle$, where $\hat{H}^{[2]}$ is the second-order expansion of $\hat{H}(x)$. From Eq. (97) we obtain the relation between the true static term and expectation values of $\hat{H}^{(1)}$ and $\hat{H}^{(2)}$:

$$\begin{aligned}\langle O(x_0)|\hat{H}^{[2]}|O(x_0)\rangle = {} & \langle O(x_0)|\hat{H}^{(2)}|O(x_0)\rangle \\ & - \langle O(x_0)|[\hat{b}^{(2)}, \hat{H}]|O(x_0)\rangle \\ & - 2\langle O(x_0)|[\hat{b}^{(1)}, \hat{H}^{(1)}]|O(x_0)\rangle \\ & + \langle O(x_0)|[\hat{b}^{(1)}, [\hat{b}^{(1)}\hat{H}]]|O(x_0)\rangle. \end{aligned} \tag{102}$$

Assuming the Brillouin conditions are fulfilled, the term $\langle O(x_0)|[\hat{b}^{(2)}, \hat{H}]|O(x_0)\rangle$ vanishes. If the natural connection is used $\langle O(x_0)|[\hat{b}^{(1)}, \hat{H}^{(1)}]|O(x_0)\rangle$ is also vanishing and the term $\langle O(x_0)|[\hat{b}^{(1)}, [\hat{b}^{(1)}\hat{H}]]|O(x_0)\rangle$ goes towards zero as the basis set increases. In this sense does the natural connection allow us to identify $\langle O(x_0)|\hat{H}^{(2)}|O(x_0)\rangle$ as the static term. If other connections are used, one must explicitly calculate all the terms of the left-hand side of Eq. (102) in order to obtain the true static term and the corresponding true response term.

6 Discussion

Within the second-quantization response formalism, calculations of molecular properties using PDBSs start by defining an orbital connection, i.e. a one-to-one correspondence between sets of orthonormal orbitals for different values x of the perturbation strength. An infinite number of connections can be constructed. This freedom can be used to identify an orbital connection, the natural connection, that gives a physical separation of the individual contributions to molecular properties. Such a physical separation is not obtained with any of the other orbital connections. To be more specific, the modified Hamiltonian in Eq. (96) is the one that is used in PDBS calculations of molecular properties calculations. This modified Hamiltonian is connection-dependent and contains, in general, contributions from basis set changes (the so-called reorthonormalization contributions) even in the limit of a complete basis set. When the natural connection is used, these contributions vanish.

Consider, for example, the calculation of magnetic properties using London orbitals. The full derivative of the Hamiltonian, $\mathrm{d}\hat{H}/\mathrm{d}B = \hat{h}^{[1]}$, becomes the angular momentum operator in the limit of a complete basis, regardless of the choice of connection. However, the operator $\hat{h}^{(1)}$, which is the one used in magnetic property calculations, only converges towards the angular momentum operator in the natural connection. The magnetizability is a sum of two terms, a static term called the diamagnetic term $\langle 0(x_0)|\hat{H}^{(2)}|0(x_0)\rangle$ and a response term called the paramagnetic term $\langle 0(x_0)^{(1)}|\hat{H}^{(1)}|0(x_0)\rangle$ where $|0(x_0)^{(1)}\rangle$ is the first-order correction to the wave function. Only the sum of these terms is connection-independent. By changing the connection one can move contributions from one term to the other. In the natural connection, the paramagnetic term has a physical interpretation since $\hat{h}^{(1)}$ converges towards the angular momentum operator. For finite basis sets the true diamagnetic term can be obtained from Eq. (102) and the true paramagnetic term can then be obtained as the difference between the total magnetizability and the true diamagnetic term. In connection with magnetic shieldings, various identifications of the diamagnetic term have been suggested. Ditchfield [5] identified the diamagnetic term as the expectation value of the operator in Eq. (98). While this is correct in the full basis set limit, it is a dubious procedure for finite basis sets. Wolinski et al. [7] used the expectation value of the second derivative of the operator in the primitive basis, i.e. the second derivative of $\langle \chi_\mu(x)|h(x)|\chi_\nu(x)\rangle$ as the diamagnetic term. This identification does not go into the correct limit when the basis set goes towards completeness.

The physical interpretation of the paramagnetic and diamagnetic terms is important as the paramagnetic term containing the angular momentum operator represents electronic contribution to the g rotational factor. This electronic contribution to the g factor can therefore be obtained rather straightforwardly with London atomic orbitals if the natural connection is used. For a general connection, the correction terms indicated in Eq. (102) must be calculated explicitly. The paramagnetic term is obtained by solving sets of linear equations. Numerical accuracy may therefore be lost if the paramagnetic term is large as may happen if the orbital connection is not chosen carefully. The optimal choice of orbital connection is of course the natural connection where the paramagnetic term does not contain reorthonormalization contributions.

We point out that when the natural connection is used, the Hamiltonian in Eq. (96) can be used to obtain time-dependent response functions and thus to calculate frequency-dependent molecular properties and their residues using perturbation-dependent basis sets. In the subsequent paper we describe how the rotational strength in circular dichrosim can be obtained as a residue of the electric dipole–magnetic dipole frequency-dependent response function using London atomic orbitals.

It should finally be noted that the original formulation of derivatives [23] does not introduce an intermediate OMO basis; the response equations are solved directly in the UMO basis. Working directly with the UMO basis does not alleviate any of the problems analyzed above. In particular, the original approach does not lead to a formalism where the true static and response terms come out naturally, and it can therefore not be used for an analysis of these terms.

Acknowledgements. This work has been partly supported by the Danish Natural Science Research Council (Grant No. 11-0924) and Nordisk Forskeruddannelsesakademi. Dr. P.-Aa. Malmqvist is thanked for very helpful comments. An anonymous referee is thanked for drawing our attention to Refs. [12, 13].

Appendix A

The equations defining the natural connection are

$$\begin{aligned} \boldsymbol{T}^{\dagger}\boldsymbol{S}\boldsymbol{T} &= 1, \\ \boldsymbol{W}\boldsymbol{T} &= \boldsymbol{T}^{\dagger}\boldsymbol{W}^{\dagger}. \end{aligned} \tag{103}$$

In order to obtain analytical derivatives of wave function and expectation values it is necessary to determine an order expansion of the connection matrix $\boldsymbol{T}$. The explicit form of $\boldsymbol{T}$ [Eq. (21)] can be expanded directly, but it is simplrr to use the above equations directly. By expanding $\boldsymbol{T}$ and $\boldsymbol{W}$ in orders of δx, the first- and second-order equations become

$$\begin{aligned} \boldsymbol{T}^{(1)} + \boldsymbol{T}^{(1)\dagger} + \boldsymbol{S}^{(1)} &= 0, \\ \boldsymbol{T}^{(1)} + \boldsymbol{W}^{(1)} &= \boldsymbol{T}^{(1)\dagger} + \boldsymbol{W}^{(1)\dagger}, \end{aligned} \tag{104}$$

$$\begin{aligned} \boldsymbol{T}^{(2)} + \boldsymbol{T}^{(2)\dagger} + \boldsymbol{S}^{(2)} + 2\boldsymbol{T}^{(1)\dagger}\boldsymbol{S}^{(1)} + 2\boldsymbol{T}^{(1)\dagger}\boldsymbol{T}^{(1)} + 2\boldsymbol{S}^{(1)}\boldsymbol{T}^{(1)} &= 0, \\ \boldsymbol{T}^{(2)} + \boldsymbol{W}^{(2)} + 2\boldsymbol{W}^{(1)}\boldsymbol{T}^{(1)} &= \boldsymbol{T}^{(2)\dagger} + \boldsymbol{W}^{(2)\dagger} + 2\boldsymbol{T}^{(1)\dagger}\boldsymbol{W}^{(1)\dagger}. \end{aligned} \tag{105}$$

Using the fact that $\boldsymbol{W}^{(1)} + \boldsymbol{W}^{(1)\dagger} = \boldsymbol{S}^{(1)}$, the first-order term of $\boldsymbol{T}$ becomes

$$\boldsymbol{T}^{(1)} = -\boldsymbol{W}^{(1)}. \tag{106}$$

The second-order term is identified from Eq. (105) as

$$\boldsymbol{T}^{(2)} = -\tfrac{1}{2}\boldsymbol{S}^{(2)} - \tfrac{1}{2}(\boldsymbol{W}^{(2)\dagger} - \boldsymbol{W}^{(2)}) + 2\boldsymbol{W}^{(1)}\boldsymbol{W}^{(1)} + \boldsymbol{W}^{(1)\dagger}\boldsymbol{W}^{(1)}. \tag{107}$$

Higher-order terms can be obtained in a similar way.

Appendix B

The exponential of an anti-Hermitian matrix with zero diagonal blocks can be expressed as

$$\exp\left(\begin{bmatrix} 0 & -\mathrm{M}^{\dagger} \\ \mathrm{M} & 0 \end{bmatrix}\right) = \begin{bmatrix} \cos(\boldsymbol{A}) & -\boldsymbol{M}^{\dagger}\sin(\boldsymbol{B})\boldsymbol{B}^{-1} \\ \boldsymbol{M}\sin(\boldsymbol{A})\boldsymbol{A}^{-1} & \cos(\boldsymbol{B}) \end{bmatrix}, \tag{108}$$

where the Hermitian matrices $\boldsymbol{A}$ and $\boldsymbol{B}$ are given by

$$\boldsymbol{A} = (\boldsymbol{M}^{\dagger}\boldsymbol{M})^{1/2}, \tag{109}$$

$$\boldsymbol{B} = (\boldsymbol{M}\boldsymbol{M}^{\dagger})^{1/2}. \tag{110}$$

To obtain Eq. (108) we have used the Taylor expansions of the exponential, cosine and sine functions. We see that the unitary matrix has Hermitian diagonal blocks and that the off-diagonal blocks are the anti-Hermitian adjoints of each other since

$$\boldsymbol{M}\sin(\boldsymbol{A})\boldsymbol{A}^{-1} = -\boldsymbol{B}^{-1}\sin(\boldsymbol{B})\boldsymbol{M}. \tag{111}$$

Moreover, any unitary matrix with Hermitian diagonal blocks may be written as the exponential of an anti-Hermitian matrix with zero elements in those blocks of the anti-Hermitian matrix in which the unitary matrix is Hermitian. This is in agreement with the fact that $2PQ$ parameters, where P and Q are the dimensions of the zero blocks, are required in order to describe an anti-Hermitian matrix with zero diagonal blocks as well as a unitary matrix with Hermitian diagonal blocks. To see the latter, recall that the number of parameters required in order to describe a unitary matrix of dimension $P + Q$ is $(P + Q)^2$. If we require the corresponding diagonal blocks of the unitary matrix to be Hermitian, we must subtract P^2 conditions for one of the blocks and Q^2 for the other, giving a total of $2PQ$ parameters.

References

1. Pulay P (19??) Adv Chem Phys 67:249
2. Helgaker T, Jørgensen P (1988) Adv quantum Chem 19:183
3. Gaw JF, Handy NC (1984) R Soc Chem Annu Rep Sect C 291
4. London F (1937) J Phys Radium 8:397
5. Ditchfield R (1972) J Chem Phys 56:5688
6. Seamans L, Linderberg J (1973) Mol Phys 24:1393
7. Wolinski K, Hinton JF, Pulay P (1990) J Am Chem Soc 112:8251
8. Helgaker T, Jørgensen P (1991) J Chem Phys 95:2595
9. Helgaker TU (1986) In: Jørgenen P, Simons J (eds) Geometrical derivatives of energy surfaces and molecular properties. Reidel, Dordrecht
10. Ruud K, Jaszunski M, Rizzo A, private communication
11. Lengsfield III BH (1986) In: Jørgenen P, Simons J (eds) Geometrical derivatives of energy surfaces and molecular properties. Reidel, Dordrecht, p 147
12. Murrell JN (1960) J Chem Phys 32:767
13. Carlson DC, Keller JM (1957) Phys Rev 105:102
14. Camp RN, King HF, Mullally DJ (1983) J Chem Phys 79:1088
15. Helgaker TU, Almölf J (1984) Int J Quantum Chem 26:275
16. Gaw JF, Handy NC (1986) In: Jørgenen P, Simons J (eds) Geometrical derivatives of energy surfaces and molecular properties. Reidel, Dordrecht, p 79
17. Helgaker T, Jørgensen P, Olsen J, Molecular electronic structure theory, to be published.
18. Olsen J (1992) In: Roos BO (eds) Lecture notes in quantum chemistry, European summer school in quantum chemistry, Lecture notes in chemistry, vol 58. Springer, Berlin, p 37
19. Linderberg J, Öhrn Y (1973) Propagators in quantum chemistry. Academic Press, New York
20. Jørgensen P, Simons J (1981) Second quantization based methods in quantum chemistry. Academic Press, New York
21. Bak KL, Jørgensen P, Jensen HJAa, Olsen J, Helgaker T (1992) J Chem Phys 97:7573
22. Bak KL, Jørgensen P, Helgaker T, Ruud K, Jensen HJAa (1993) J Chem Phys 98:8873
23. Gerratt J, Mills IM J Chem Phys 49:1719