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Many-body theory of multiple core holes

L. S. Cederbaum*
The Fritz Haber Research Center for Molecular Dynamics, The Hebrew University of Jerusalem,
91904 Jerusalm, Israel

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The response of an electronic system to the creation of double and multiple core vacancies is investigated. Under certain conditions the calculations are considerably simplified and a linked-cluster theorem can be formulated for the corresponding core-hole spectra. Particular attention is paid to the relation of properties of double and multiple core holes to those of the well-studied single core holes.

I. INTRODUCTION

A vast number of experimental and theoretical work exists on the properties of core holes in atoms, molecules, solids, and chemisorbed systems.[1-4] Most of the work has been concerned with the determination of the core-hole binding energies and the response of the system to the sudden creation of a vacancy in the core. Improved experimental techniques[5] and the availability of synchrotron radiation prove useful for investigating the dynamics of the core-hole creation and lead to new activities in the field.

In contrast to the creation of single core holes only little attention has been paid to the creation of multiple vacancies and in particular to multiple core holes. Two-electron—one-photon processes have been reported on inert gases.[6-9] For Ar it has been found[9] that the cross section for the $K^{-1}M^{-1}$ double vacancy is only one order of magnitude below that of the K^{-1} single vacancy. Multiple vacancies in solids have been investigated recently[10-14] showing that the cross section for the creation of double core holes decreases relative to that of single core holes with increasing atomic number.

The fact that double core holes could be studied even for heavier atoms indicates that such vacancies can be investigated experimentally for molecules, where, to the knowledge of the author, no results are available yet. In contrast to atoms, molecules have the additional advantage that the various core vacancies can be localized at different atomic sites. First numerical results[15] on the energies of molecular double core vacancies indeed demonstrate that if the vacancies are at different atomic sites, one is probing the chemical environment of these atoms much more sensitively than in single-core-vacancy situations. In particular, double-core-hole spectroscopy should provide interesting information on the bonding properties in gas phase and chemisorbed molecules, molecular crystals, and heteronuclear solids.

In the present manuscript the many-body theory associated with the sudden creation of multiple core holes is investigated making explicit use of the genuine properties of core levels. The relevant Hamiltonian is discussed in Sec. II and the spectrum, or equivalently, the various core Green's functions, in Sec. III. Section IV is devoted to the evaluation of the spectrum and some properties of the spectrum are compared in Sec. V to those of the single-core-hole spectrum.

II. THE CORE-VALENCE HAMILTONIAN

The Hamiltonian of an electronic system reads

$$H=\sum_i \varepsilon_i a_i^\dagger a_i+\sum_{i,j} v_{ij} a_i^\dagger a_j+\tfrac{1}{2}\sum_{i,j,k,l} V_{ijkl} a_i^\dagger a_j^\dagger a_l a_k \qquad (1)$$

where ε_i, v_{ij}, and V_{ijkl} are the matrix elements of an unperturbed Hamiltonian, a one-particle potential v which can, in principle, include an external potential, and of the electron Coulomb interaction

$$V_{ijkl}=\langle \phi_i(r)\phi_j(r') \mid |r-r'|^{-1} \mid \phi_k(r)\phi_l(r')\rangle ,$$

respectively $\{\phi_i\}$ denotes any complete orthonormal basis of spin orbitals that diagonalizes the unperturbed Hamiltonian and $\{a_i\}$ is the corresponding set of annihilation operators.

The general Hamiltonian (1) can be simplified by making explicit use of the genuine properties of core electrons. Because of the large difference in energy and in the localization in space of core and valence electrons, it is commonly accepted that the eigenstates of the system can be separated to a good approximation into a core and a valence part. Imposing this separability of core and valence electrons, the Hamiltonian (1) reduces to the simpler core-valence Hamiltonian H_{cv} which, for a single spatial core orbital of its kind, takes on the following appearance:[16]

$$H_{cv}=H_v+H_c+F_{cv}+W_{cv} \ . \qquad (2)$$

The operator H_v denotes the Hamiltonian of the valence electrons. Choosing for convenience the Hartree-Fock operator as the unperturbed Hamiltonian in (1), the ϕ_i and ε_i become the Hartree-Fock orbitals and orbital energies and H_v reads

$$H_v = H_0 + V_v \ ,$$

$$H_0 = \sum_i \varepsilon_i a_i^\dagger a_i \ , \tag{3a}$$

$$V_v = -\sum_{i,j}\left[\sum_k (V_{ikjk} - V_{ikkj}) n_k\right] a_i^\dagger a_j + \tfrac{1}{2}\sum_{i,j,k,l} V_{ijkl} a_i^\dagger a_j^\dagger a_l a_k ,$$

where here and in the following all the indices i, j, k, and l do *not* include the core index c. The occupation number n_k of the orbital ϕ_k equals 1 (0) if ϕ_k is occupied (unoccupied) in the Hartree-Fock ground state. The Hamiltonian H_c describes the core electrons and is given by

$$H_c = \varepsilon_c(\hat{n}_{c\uparrow} + \hat{n}_{c\downarrow}) + V_{cccc}\hat{n}_{c\uparrow}\hat{n}_{c\downarrow} + v_{cc}(\hat{n}_{c\uparrow} + \hat{n}_{c\downarrow}) \ , \tag{3b}$$

where $\hat{n}_m = a_m^\dagger a_m$ is the occupation-number operator and the one-electron spin indices are denoted by ↑ and ↓. There are two terms describing the interaction of the valence and core electrons. The spin-flip term F_{cv} may not preserve the spin of the core electrons,

$$F_{cv} = \left[-\sum_{i,j} V_{ic\uparrow c\downarrow j} a_i^\dagger a_j\right] a_{c\uparrow}^\dagger a_{c\downarrow} + \text{H.c.} \ , \tag{3c}$$

and the second, more relevant interaction term takes on the form

$$W_{cv} = -(1-\hat{n}_{c\uparrow}) \sum_{i,j} (V_{ic\uparrow jc\uparrow} - V_{ic\uparrow c\uparrow j}) a_i^\dagger a_j + (c\uparrow \to c\downarrow) \ . \tag{3d}$$

The full Hamiltonian H as well as the core-valence Hamiltonian H_{cv} commute with the spin operators $\hat{S}_z$ and $\hat{S}^2$ and also with the electron-number operator $\hat{N} = \sum_m \hat{n}_m$. The latter Hamiltonian commutes, moreover, separately with the core-electron-number operator $\hat{N}_c = \hat{n}_{c\uparrow} + \hat{n}_{c\downarrow}$ and valence-electron-number operator $\hat{N}_v = \sum_i \hat{n}_i$ owing to the imposed core-valence separability. Obviously, $\hat{N} = \hat{N}_c + \hat{N}_v$. The correct spin symmetry of the states arising due to the creation of core vacancies is established by the spin-flip term. On the other hand, the matrix elements of F_{cv} are small, since they describe the exchange interaction of core and valence electrons. F_{cv} can be neglected in many situations and, if necessary, its effect can be taken subsequently into account. Once the spin-flip term is neglected, the core-valence Hamiltonian H_{cv} commutes also with $\hat{n}_{c\uparrow}$ and $\hat{n}_{c\downarrow}$. Consequently, we may substitute these core-occupation-number operators by numbers 1 or 0 according to the occupancy of the core orbitals. In the ground state all core orbitals are occupied, we have $n_{c\uparrow} = n_{c\downarrow} = 1$ and thus W_{cv} vanishes and the core and valence parts do not interact beyond the Hartree-Fock level. If one or two core holes are created, one or both of the operators $\hat{n}_{c\uparrow}$ and $\hat{n}_{c\downarrow}$ are put to zero and the valence electrons now react to a one-particle potential W_{cv} in addition to the potential V_v in Eq. (3a) describing the usual interaction between the valence electrons. The combination of both W_{cv} and V_v renders the single- or multiple-core-hole problem a "true" many-body problem. It should be mentioned that H_{cv} does not describe the decay of the core vacancies via x-ray and Auger emission since the number of core electrons is preserved. Very often one may treat this decay by first calculating the stationary states and subsequently computing the line broadening using perturbation theory.[17,18]

The presence of additional atoms with core orbitals complicates somewhat the situation, in particular when core orbitals are delocalized over several equivalent atomic sites due to symmetry requirements. However, in any case of (deep) core electrons one may express the localized core orbitals ϕ_{c_k}, $k = 1,2,\ldots,$ as a superposition of nonsymmetry-adapted core orbitals ϕ_{s_n}, $n = 1,2,\ldots,$ each localized at its atomic site n. In the basis of such localized core orbitals the *general* core-valence Hamiltonian takes on the following form, independently of whether the system contains equivalent atomic sites:

$$H_{cv} = H_v + \sum_n H_{s_n}^v + \sum_{\substack{m,n \\ (m>n)}} W_{s_n s_m} + \sum_{\substack{m,n \\ (m>n)}} W_{s_n s_m}^v \ . \tag{4}$$

The operator H_v is the Hamiltonian of the valence electrons given in Eq. (3a) and $H_{s_n}^v$ is defined throughout the operator $H_{s_n v}$

$$H_{s_n v} = H_v + H_{s_n}^v \ , \tag{5a}$$

which is the Hamiltonian of the system with one active localized core orbital ϕ_{s_n} and is given by H_{cv} in Eq. (2) with $c = s_n$. The sum of the first two terms on the right-hand side of Eq. (4) thus constitutes the core-valence Hamiltonian with independent[19] core electrons. The core electrons on different atomic sites may interact directly by the trivial electrostatic repulsion term

$$W_{s_n s_m} = V_{s_n s_m s_n s_m} \hat{N}_{s_n} \hat{N}_{s_m} \ , \tag{5b}$$

where $\hat{N}_{s_n} = \hat{n}_{s_n\uparrow} + \hat{n}_{s_n\downarrow}$ is the core-electron-number operator at the atomic site n, or indirectly via the valence electrons by the term

$$\begin{aligned} W_{s_n s_m}^v = \Bigg[& \left[-\sum_{i,j} V_{is_n\uparrow s_m\uparrow j} a_i^\dagger a_j\right] a_{s_n\uparrow}^\dagger a_{s_m\uparrow} + (s\uparrow \to s\downarrow) \\ & + \left[-\sum_{i,j} V_{is_n\uparrow s_m\downarrow j} a_i^\dagger a_j\right] a_{s_n\uparrow}^\dagger a_{s_m\downarrow} \\ & + (s\uparrow \leftrightarrow s\downarrow) \Bigg] + \text{H.c.} \end{aligned} \tag{5c}$$

The term (5c) describes how a core hole may hop from one atomic site to another. Similarly to the spin-flip term, this hopping term contains only exchange matrix elements between core and valence electrons and represents, therefore, a weak interaction. The term $W_{s_n s_m}^v$ can be safely neglected when the sites n and m are occupied by atoms of a different kind, e.g., carbon and nitrogen atoms. It will be shown in Sec. III that even when the sites n and m are occupied by the same kind of atoms, the interaction $W_{s_n s_m}^v$ is by far less important than the spin-flip terms $F_{s_n v}$. Neglecting the hopping terms, the resulting core-valence Hamiltonian commutes with the $\hat{N}_{s_n}$ and if the spin-flip terms are omitted as well, H_{cv} commutes with each of the core occupation number operators $\hat{n}_{s_n\uparrow}$ and $\hat{n}_{s_n\downarrow}$, $n=1,2,\ldots$. Consequently, we may, as in the case of a single atom, replace these operators by numbers according to the occupancy of core electrons in a given state. Once this occupancy is defined in a given situation, the problem can be reduced to the treatment of the valence electrons alone. The potential seen by these electrons depends solely on the core vacancies introduced at specific atoms and not on the core electrons localized on the other atoms.

III. THE MULTIPLE-CORE-HOLE SPECTRUM

Green's functions[20,21] provide a powerful tool to obtain information on the electronic system undergoing a sudden change in the number of core electrons. The one-particle Green's function, for example, reads[20,21]

$$G_{mn}(t)=-i\langle\psi_0^N\,|\,T\{a_m(t)a_n^\dagger\}\,|\,\psi_0^N\rangle\ , \tag{6a}$$

where ψ_0^N denotes the ground-state wave function of the N-electron system and T is the Wick time-ordering operator. Using the core-valence Hamiltonian (2) this Green's function reduces to (a closed-shell system is assumed)

$$G_{cc}(t)\equiv G_{c\uparrow c\uparrow}(t)=G_{c\downarrow c\downarrow}(t)=i\langle\psi_0^N\,|\,a_c^\dagger a_c(t)\,|\,\psi_0^N\rangle \tag{6b}$$

for $t\leq 0$ and vanishes for $t>0$. At time $t\leq 0$ a core electron is ejected out of the system and returned to the system at a later time ($t=0$). $G_{cc}(t)$ describes the probability amplitude in recovering the initial state $|\,\psi_0^N\rangle$ as a function of time. The core-hole spectrum $P(\omega)$ as a function of energy ω is defined by

$$\begin{aligned}P(\omega)&\simeq\mathrm{Im}G_{cc}(\omega)\\&\simeq\int_{-\infty}^{\infty}dt\,e^{i(\omega-E_0^N)t}\langle\psi_0^N\,|\,a_c^\dagger e^{iH_{cv}t}a_c\,|\,\psi_0^N\rangle\ ,\end{aligned} \tag{7}$$

where $G_{cc}(\omega)$ is the Fourier transform of $G_{cc}(t)$ and E_0^N is the ground-state energy. The core-hole spectrum (7) is indeed closely related to an experimentally measurable spectrum. The ionization spectrum of an electronic system obtained by photon or electron impact reduces under the conditions of the sudden approximation[22,23] to $P(\omega)$ in the above equation.[24,25]

Analogously, the two-particle, three-particle, etc., Green's function and the corresponding spectra may be introduced to describe the sudden simultaneous ejection of two, three, or even more core electrons. To be specific we discuss in the following the case of two core electrons. The results can be straightforwardly extended to describe more core electrons. It suffices to consider two spatial core orbitals carrying the indices s_1 and s_2. The annihilation of two core electrons in a closed-shell system leads to dicationic states of either singlet or triplet character. There are several two-particle Green's functions relevant for the double-core-hole spectrum. They can be defined in analogy to Eq. (6),

$$\mathcal{G}_{mn}(t)=-i\langle\psi_0^N\,|\,T\{b_m(t)b_n^\dagger\}\,|\,\psi_0^N\rangle\ , \tag{8a}$$

where the b_m now refer to products of core annihilation operators introduced in the following:

$$\begin{aligned}&b_1=a_{s_1\uparrow}a_{s_1\downarrow},\ \ b_2=a_{s_2\uparrow}a_{s_2\downarrow},\ \ b_3=a_{s_1\downarrow}a_{s_2\downarrow}\ ,\\&b_{4,5}=\frac{1}{\sqrt{2}}(a_{s_1\downarrow}a_{s_2\uparrow}\pm a_{s_1\uparrow}a_{s_2\downarrow}),\ \ b_6=a_{s_1\uparrow}a_{s_2\uparrow}\ .\end{aligned} \tag{8b}$$

Application of the three operators b_1, b_2, and b_4 on the ground states gives rise to dicationic singlet states whereas the remaining operators correspondingly lead to triplet states. The operators b_1 and b_2 create double core vacancies where both vacancies are at the same atomic site and thus possess different properties than the other operators which create two vacancies each at a different atomic site. We denote the corresponding double-core-hole states by s_1^{-2}, s_2^{-2}, and $s_1^{-1}s_2^{-1}$.

The 36 Green's functions $\mathcal{G}_{mn}$ introduced above are not independent of each other. In particular, the three "triplet" functions $\mathcal{G}_{33}$, $\mathcal{G}_{55}$, and $\mathcal{G}_{66}$ are essentially identical and represent the magnetic quantum number $M=1$, 0, and -1, respectively, of the triply degenerate dicationic states. Obviously, all nondiagonal Green's functions $\mathcal{G}_{mn}$, $m\neq n$, where the operators b_m and b_n correspond to different spin quantum numbers of the resulting dicationic states, vanish. Furthermore, the functions $\mathcal{G}_{mn}$ and $\mathcal{G}_{nm}$ contain the same information. We are thus left with seven distinct Green's functions $\mathcal{G}_{11}$, $\mathcal{G}_{22}$, $\mathcal{G}_{33}$, $\mathcal{G}_{44}$, $\mathcal{G}_{12}$, $\mathcal{G}_{14}$, and $\mathcal{G}_{24}$ out of which the latter three contribute only little to the double-core-hole spectrum as will be seen below. In the special situation where the two atomic sites are equivalent by symmetry, we furthermore find $\mathcal{G}_{11}$ and $\mathcal{G}_{22}$ to be essentially identical (if the point group to which the system belongs contains degenerate irreducible representations and more equivalent sites are present, the situation is somewhat more subtle).

The most general double-core-hole spectrum is obtained by introducing a "transition operator" $\mathcal{T}$ as a superposition of the double annihilation operators b_n, $n=1-6$, with amplitude τ_n according to

$$\mathcal{T}=\sum_{n=1}^{6}\tau_n b_n\ . \tag{9}$$

The double-core-hole spectrum thus obtained reads

$$P(\omega)\simeq\int_{-\infty}^{\infty}dt\,e^{i\omega t}\langle\psi_0^N\,|\,\mathcal{T}^\dagger\mathcal{T}(t)\,|\,\psi_0^N\rangle\ , \tag{10a}$$

$$\mathcal{T}(t)=e^{iH_{cv}t}\mathcal{T}e^{-iH_{cv}t}\ . \tag{10b}$$

This spectrum is of relevance since the poles of the Green's functions involved explicitly exhibit the energies needed to create the various double-core-hole states and the corresponding residues contain important information about the wave functions. There is also a possible experimental realization of the above spectrum. The impact of a fast charged particle on the system may lead to the simultaneous ejection of two core electrons described by Eq. (10).

The evaluation of the spectrum (10) is simplified by noting that the operation of the core-valence Hamiltonian (4) on the various $b_n\,|\,\psi_0^N\rangle$ can be written as

$$H_{cv}b_n\,|\,\psi_0^N\rangle=\sum_{m=1}^{6}\mathcal{H}_{mn}b_m\,|\,\psi_0^N\rangle\ , \tag{11}$$

where the $\mathcal{H}_{mn}$ are operators operating on the valence electrons only and thus commute with the b_n. This finding can be used to eliminate all the core electrons from the Green's functions and, in particular, from the expression (10) of the spectrum. The resulting functions and spectrum then depend solely on the coordinates of the valence electrons. With the aid of Eq. (11) the spectrum (10) takes on the form

$$P(\omega)\simeq \int_{-\infty}^{\infty} dt\, e^{i(\omega-E_0^{N_v})t}\tau^\dagger\langle \psi_0^{N_v} | e^{i\mathscr{H}t} | \psi_0^{N_v}\rangle\tau , \tag{12}$$

where $\mathscr{H}$ is a six-dimensional matrix Hamiltonian with elements $\mathscr{H}_{nm}$ acting in the space of valence electrons and τ is a column vector with the amplitude τ_n, $n=1$–6, as elements. The quantities $E_0^{N_v}$ and $\psi_0^{N_v}$ are the ground-state energy and wave function of the valence electrons only, i.e., $H_v\psi_0^{N_v}=E_0^{N_v}\psi_0^{N_v}$. It should be mentioned that the various Green's functions introduced in Eq. (8) can be obtained from the spectrum (12) by evaluating this spectrum for specific values of the τ_n, e.g., by putting $\tau_1=1$ and all the other $\tau_n=0$ we obtain the imaginary part of $\mathscr{G}_{11}(\omega)$ out of which also the real part can be determined by applying well-known relations.[20,26]

The matrix Hamiltonian $\mathscr{H}$ can be explicitly expressed in terms of the auxilary operators

$$Q^{ab}_{\gamma\gamma'}=\sum_{i,j} V_{is_a\gamma s_b\gamma' j}a^\dagger_{i\gamma'}a_{j\gamma};\quad a,b=1,2;\quad \gamma,\gamma'=\uparrow\downarrow . \tag{13a}$$

In order to elucidate the origin of the individual terms, we collect them in groups arising from different interaction operators in the core-valence Hamiltonian,

$$X_\pm=\frac{1}{\sqrt{2}}(Q^{22}_{\downarrow\uparrow}\pm Q^{11}_{\downarrow\uparrow}),\quad Y=\tfrac{1}{2}(Q^{11}_{\downarrow\downarrow}-Q^{11}_{\uparrow\uparrow}+Q^{22}_{\uparrow\uparrow}-Q^{22}_{\downarrow\downarrow}) ,$$

$$Z_{\gamma\gamma'}=Q^{12}_{\gamma\gamma'},\quad Z_\pm=\frac{1}{\sqrt{2}}(Z_{\uparrow\uparrow}\pm Z_{\downarrow\downarrow}) . \tag{13b}$$

The quantities $X_\pm$ and $Z_{\gamma\gamma'}$ appear in the spin-flip and hopping operators $F_{s_a v}$ and $W^{v}_{s_1 s_2}$, respectively, discussed in detail in Sec. II. The quantity Y originates from the exchange part of the potential seen by the valence electrons when a vacancy is created in the orbital $\phi_{s_a\gamma}$. As mentioned in Sec. II, this potential is determined by putting $\hat{n}_{s_a\gamma}=0$ in $W_{s_a v}$, see Eq. (3d). We define the potential for the valence electrons ($\gamma=\uparrow$)

$$\begin{aligned} V_{a\uparrow}= {}& W_{s_a v}(\hat{n}_{s_a\uparrow}=0,\hat{n}_{s_a\downarrow}=1)\\ & -\langle W_{s_a v}(\hat{n}_{s_a\uparrow}=0,\hat{n}_{s_a\downarrow}=1)\rangle , \end{aligned} \tag{14a}$$

where $\langle W\rangle$ is the average value of the operator W in the unperturbed (here, Hartree-Fock) ground state, and obtain

$$V_{a\uparrow}=-\sum_{i,j}(V_{is_a\uparrow js_a\uparrow}-V_{is_a\uparrow s_a\uparrow j})(a_i^\dagger a_j-n_i\delta_{ij}) . \tag{14b}$$

Of course, a potential $V_{a\downarrow}$ defined analogously is obtained by setting $\gamma=\downarrow$.

The matrix Hamiltonian now takes on the appearance

$$\left(\begin{array}{cc|cccc} H_{11}(\uparrow\downarrow) & 0 & -Z_{\uparrow\downarrow} & -Z_- & -Z_+ & Z_{\downarrow\uparrow} \\ & H_{22}(\uparrow\downarrow) & Z^\dagger_{\downarrow\uparrow} & Z^\dagger_- & -Z^\dagger_+ & -Z^\dagger_{\uparrow\downarrow} \\ \hline & & H_{12}(\downarrow\downarrow) & X_+ & X_- & 0 \\ & & & H_{12}(\uparrow\downarrow) & Y & X_+ \\ & & & & H_{12}(\downarrow\uparrow) & -X_- \\ & & & & & H_{12}(\uparrow\uparrow) \end{array}\right) . \tag{15a}$$

Since the matrix Hamiltonian is Hermitian, there is no need to explicitly show the lower triangle in Eq. (15a). The diagonal elements of $\mathscr{H}$ read

$$\begin{aligned} H_{ab}(\gamma\gamma')= {}& -\varepsilon_{s_a}-\varepsilon_{s_b}+V_{s_a s_b s_a s_b}+H_v\\ & +\tfrac{1}{2}(V_{a\gamma}+V_{a\gamma'}+V_{b\gamma}+V_{b\gamma'}) , \end{aligned} \tag{15b}$$

where $a\,(b)=1,2$ and $\gamma(\gamma')=\uparrow,\downarrow$.

Because of the core-valence separability we have been able to eliminate all core operators from the expressions for the Green's functions or, equivalently, from the expression for the single-, double-, or multiple-core-hole spectrum. Core properties enter only through the orbital energies ε_{s_n}, the electrostatic repulsion integrals $V_{s_n s_m s_n s_m}$ and, most importantly, through the Coulomb and exchange integrals $V_{is_n js_n}$ and $V_{is_n s_m j}$. In the case of the production of double core vacancies, the resulting matrix Hamiltonian (15a) describes the motion of the valence electrons in the field of two core holes. The problem becomes intricate because of the additional intrinsic interaction of the valence electrons and the indirect interaction of the double-core-hole configurations. As can be seen from Eqs. (15a) and (13), the latter interaction contains only exchange integrals of core and valence orbitals and is thus of secondary importance.

The nondiagonal elements of $\mathscr{H}$ in (15a) are of varying relevance. The matrix Hamiltonian has been divided into two parts as indicated in Eq. (15a). The upper left corner of $\mathscr{H}$ describes double core holes where the two vacancies are at the same atom. Since $\mathscr{H}_{12}=0$, there is no direct coupling between the s_1^{-2} and s_2^{-2} vacancies and the double vacancy at one site can only hop to the other atomic site through the indirect coupling to the vacancies of the

$s_1^{-1}s_2^{-1}$ type. Because of the substantial energy gap between the two types of vacancies and the smallness of the matrix elements of Z, we may put $\mathscr{G}_{12}(t)=\mathscr{G}_{21}(t)=0$ to an excellent approximation and even neglect all the coupling $Z_{\uparrow\downarrow}$, $Z_{\downarrow\uparrow}$, and $Z_{\pm}$ between the s_n^{-2} and $s_1^{-1}s_2^{-1}$ vacancy types. The above-mentioned energy gap is dictated, for a given atomic species, by the difference in electrostatic repulsion energy $V_{s_n s_n s_n s_n}$ and $V_{s_1 s_2 s_1 s_2}$ appearing in the diagonal elements of $\mathscr{H}$, see Eq. (15b). The latter energy depends on the internuclear distance between the atomic sites involved and is of the order of 10 eV or less. The former energy is the repulsion energy of two core electrons at the same atomic site and amounts to about 100 eV already for an atom as light as a carbon atom. If desired, the influence of the $Z_{\uparrow\downarrow}$, $Z_{\downarrow\uparrow}$, and $Z_{\pm}$ operators can be taken into account by straightforward perturbation theory.

The lower right corner $\overline{\mathscr{H}}$ of $\mathscr{H}$ in (15a) describes the valence electronic motion following the creation of a double core hole $s_1^{-1}s_2^{-1}$ where each vacancy is located at a different atomic site. The infinitely many eigenstates of this four-dimensional Hamiltonian $\overline{\mathscr{H}}$ can be arranged in a series of four closely related states, a threefold degenerate dicationic triplet and a dicationic singlet. If the nondiagonal elements of $\overline{\mathscr{H}}$ are neglected, most of the resulting eigenstates will not be eigenstates of the spin operator. The states which derive from the unperturbed double vacancy with no valence electrons excited, the so-called *main states*, are only slightly affected by the nondiagonal elements of $\overline{\mathscr{H}}$. Numerical calculations[15] on the double core vacancies of acteylene show that the energy difference between the singlet and triplet states is rather small. These computations have been carried out twice, with and without imposing the core-valence separability, demonstrating the usefulness of assuming this separability in evaluating double core vacancies.

The states which, on the unperturbed level of approximation, are described by a double core vacancy accompanied by an excitation of the valence electrons, the so-called *satellite states*, are stronger affected by the coupling in $\overline{\mathscr{H}}$ than the main states. Without the coupling elements in $\overline{\mathscr{H}}$ there appear degeneracies and quasidegeneracies of the satellite states which are partly lifted by introducing these couplings and vice versa. Since the coupling operators are "weak," we may determine their effect by using low-order and low-dimension quasidegenerate perturbation theory once the states of the diagonal elements of $\overline{\mathscr{H}}$ are known.

The double-core-hole spectrum (12) becomes a superposition of six spectra $P_n(\omega)$ if the matrix Hamiltonian $\mathscr{H}$ is assumed diagonal,

$$P_n(\omega)\simeq\int_{-\infty}^{\infty}dt\, e^{i(\omega-E_0^{N_v})t}\langle\psi_0^{N_v}|e^{i\mathscr{H}_{nn}t}|\psi_0^{N_v}\rangle\ , \qquad (16)$$

where the explicit form of the operators $\mathscr{H}_{nn}$, $n=1$–6, is given in Eq. (15b). As can be inferred from Eq. (15b), the spectra or, equivalently, the corresponding Green's function $\mathscr{G}_{nn}(\omega)$ are not independent of each other. One rather finds the following relations:

$$\begin{aligned}&P_3(\omega)=P_6(\omega),\ \ P_4(\omega)=P_5(\omega)\ ,\\&\mathscr{G}_{33}(\omega)=\mathscr{G}_{66}(\omega),\ \ \mathscr{G}_{44}(\omega)=\mathscr{G}_{55}(\omega)\ ,\\&\mathscr{G}_{nm}(\omega)=0,\ \ n\neq m\end{aligned} \qquad (17)$$

and if the two sites s_1 and s_2 are equivalent by symmetry requirements, also $P_1(\omega)=P_2(\omega)$. The above relations formally contradict the exact findings discussed above in that the triplet spectrum $P_5(\omega)$ is not equal to the other triplet spectra $P_3(\omega)$ and $P_6(\omega)$, but rather equals the singlet spectrum $P_4(\omega)$. This is not surprising in view of the fact that, as discussed in Sec. II, we have abandoned spin symmetry by neglecting the spin-flip term. In Eq. (17), $P_4(\omega)$ and $P_5(\omega)$ simulate an averaged singlet-triplet spectrum. Inclusion of the interaction terms will produce a "split" of states leading to the exact result $\mathscr{G}_{33}=\mathscr{G}_{66}=\mathscr{G}_{55}\neq\mathscr{G}_{44}$. However, as mentioned above, the quantitative effect of the interaction terms is rather small and may be neglected in many cases or, if desired, computed subsequently.

Alternatively one may, of course, evaluate the full spectrum (12) via a configuration-interaction calculation for the matrix Hamiltonian $\mathscr{H}$ or $\overline{\mathscr{H}}$ similarly to the case of vibronic coupling in molecules.[27] To this end one can use the eigenfunctions $\psi_m^{N_V}$ of the valence Hamiltonian H_v to construct a supermatrix with 4×4 matrices $\langle\psi_m^{N_v}|\overline{\mathscr{H}}|\psi_n^{N_v}\rangle$ as elements. This supermatrix decouples into four submatrices out of which three, representing the triplet dicationic states, are essentially identical. The eigenvalues of the submatrices give the positions of the lines in the spectrum and the square of the first element of the corresponding eigenvector multiplied by the appropriate $|\tau_n|^2$ yields the intensities of these lines. This method is numerically elaborate in particular if many lines of the spectrum are to be calculated.

In Sec. IV we attempt the evaluation of the double-core-hole spectrum neglecting the nondiagonal elements of $\mathscr{H}$ in Eq. (15a). These nondiagonal elements contain only exchange integrals $V_{is_n s_m j}$ between core and valence electrons. The Hamiltonians appearing as the diagonal elements of $\mathscr{H}$ contain the more important Coulomb integrals $V_{is_n js_m}$, but also exchange integrals $V_{is_n s_n j}$. The question may arise, why not neglect the latter exchange integrals as well and thus simplify the evaluation of the spectrum? It can be shown, however, that the errors introduced by neglecting the exchange integrals in the diagonal of $\mathscr{H}$ are substantially larger than those encountered by neglecting them in the nondiagonal part of $\mathscr{H}$. In second-order-perturbation theory, for instance, products of Coulomb and exchange integrals are neglected in the first case, while in the second case only products of exchange integrals are omitted [see also explicit expressions, Eqs. (18a) and (18b), in Ref. (16) for the single-core-hole situation].

IV. EVALUATION OF THE SPECTRUM

The single-, double-, etc., core-hole spectrum can be rewritten to be the Fourier transform of the ground-state autocorrelation function of a matrix Hamiltonian operating only in the space of the valence electrons. The dimension of the matrix Hamiltonian is given by the number of possibilities to create a single-, double-, etc., core vacancy under consideration. We begin here with the evaluation of the double-core-hole spectrum and concentrate first on the case of the two vacancies being located at the same atomic site. Following the discussion of Sec. III we may, because of the small matrix elements of the hopping operator $W^{v}_{s_n s_m}$ and the large energy gaps involved, neglect the presence of possible core orbitals on other atoms and consider one active atomic site only. The core-valence Hamiltonian to be considered is given by Eqs. (2) and (3). Since the spin-flip operator has zero effect when operating on the ground state $|\psi_0^N\rangle$ as well as on $a_{c\uparrow}a_{c\downarrow}|\psi_0^N\rangle$, it can be omitted in an *exact* manner. Consequently, we are left with the problem of calculating $P_1(\omega)$ or, equivalently, $\mathcal{G}_{11}(\omega)$, see Eqs. (17) and (18), using the Hamiltonian $H_{11}(\uparrow\downarrow)$ defined in Eq. (15b) which does not contain the spin-flip operator (notice that, for convenience, we put $c=s_1$).

It is a central result of the quantum theory of many-particle systems that the various Green's functions and other relevant quantities like the vacuum amplitude[28] can be expanded in Feynman diagrams.[20,21] We introduce in Fig. 1 the symbols we use in the diagrammatic expansion of the Green's functions and vacuum amplitude. The straight line shown in this figure represents the so-called free *one-particle* Green's function given explicitly by (m and n are one-particle indices)

$$G^0_{mn}(t)=i\delta_{mn}e^{-i\varepsilon_m t}[\Theta(-t)n_m-\Theta(t)(1-n_m)]\ , \quad (18)$$

where $\Theta(t)$ is the usual step function. A straight line pointing downwards, i.e., $t\leq 0$ and $n_m=1$, is called a hole line and a line pointing upwards, i.e., $t>0$ and $n_m=0$, is referred to as a particle line. For the details of drawing and evaluating the diagrams of a given quantity we refer readers to textbooks.[20,21,28] The diagrams of $\mathcal{G}_{11}(t)$ up to second order are explicitly shown in Fig. 2.

The Green's function $\mathcal{G}_{11}(t)$ for the double core hole s_1^{-2} can be written as[28]

$$\mathcal{G}_{11}(t)=\lim_{\substack{T_1\to-\infty\\ T_2\to+\infty}} Q(T_2,T_1,t)\ , \quad (19a)$$

where

$$Q=-i\frac{\langle\phi_0^N|T[\tilde{U}(T_2,T_1)\bar{b}_1(t)\bar{b}_1^\dagger]|\phi_0^N\rangle}{\langle\phi_0^N|\tilde{U}(T_2,T_1)|\phi_0^N\rangle}\ , \quad (19b)$$

ϕ_0^N is the unperturbed ground-state (here Hartree-Fock) wave function, $\bar{b}_1$ denotes the operator b_1 [see Eq. (8b)] in the interaction picture, and $\tilde{U}$ is the time-development operator for the core-valence Hamiltonian H_{cv}. In analogy to the single-core-hole situation,[16] the core operators can be eliminated from the expression (19b). We introduce two time-development operators $U_0(T_2,T_1)$ and $U_t(T_2,T_1)$, operating only in the space of valence electrons, for the Hamiltonians H_v and the *time-dependent* Hamiltonian $H_v+V_1(t')$, respectively, where

$$V_1(t')=(V_{1\uparrow}+V_{1\downarrow})\Theta(t'-t)\Theta(-t') \quad (20)$$

and the interactions $V_{1\uparrow}$ and $V_{1\downarrow}$ have been defined in Eq. (14b). It now follows that

$$Q=ie^{-i(2\varepsilon_{s_1}-V_{s_1s_1s_1s_1})t}R_t(T_2,T_1)/R_0(T_2,T_1)\ , \quad (21)$$

where R_0 and R_t are vacuum amplitudes[28] for different perturbations of the valence electrons,

$$R_0(T_2,T_1)=\langle\phi_0^{N_v}|U_0(T_2,T_1)|\phi_0^{N_v}\rangle\ , \quad (22a)$$

$$R_t(T_2,T_1)=\langle\phi_0^{N_v}|U_t(T_2,T_1)|\phi_0^{N_v}\rangle\ , \quad (22b)$$

$\phi_0^{N_v}$ is the unperturbed ground-state wave function of the valence electrons.

The vacuum amplitudes are subject to the well-known linked-cluster theorem[28]

$$R_0(T_2,T_1)=\exp[C_0(T_2,T_1)]\ , \quad (22c)$$

$$R_t(T_2,T_1)=\exp[C_t(T_2,T_1)]\ , \quad (22d)$$

The functions C_0 and C_t are given by the sum of all *connected* diagrams of R_0 and R_t, respectively. Introducing their difference

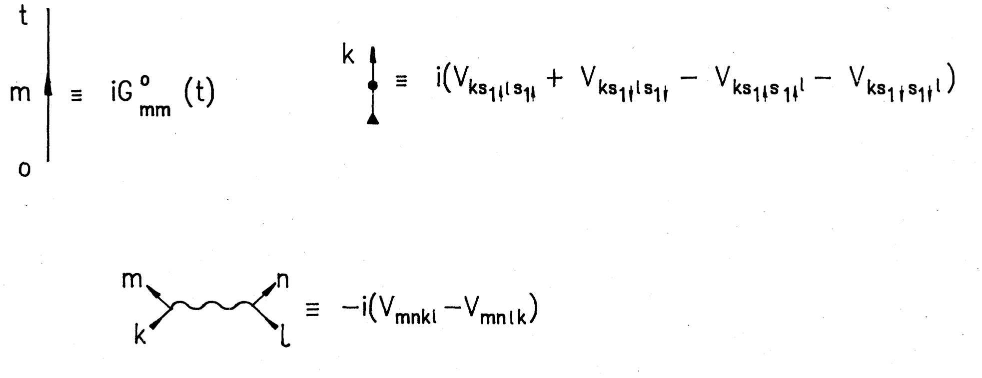

FIG. 1. The definition of the symbols used in the diagrammatic expansion of the two-particle Green's function $\mathcal{G}_{11}(t)$ defined in Eq. (8a).

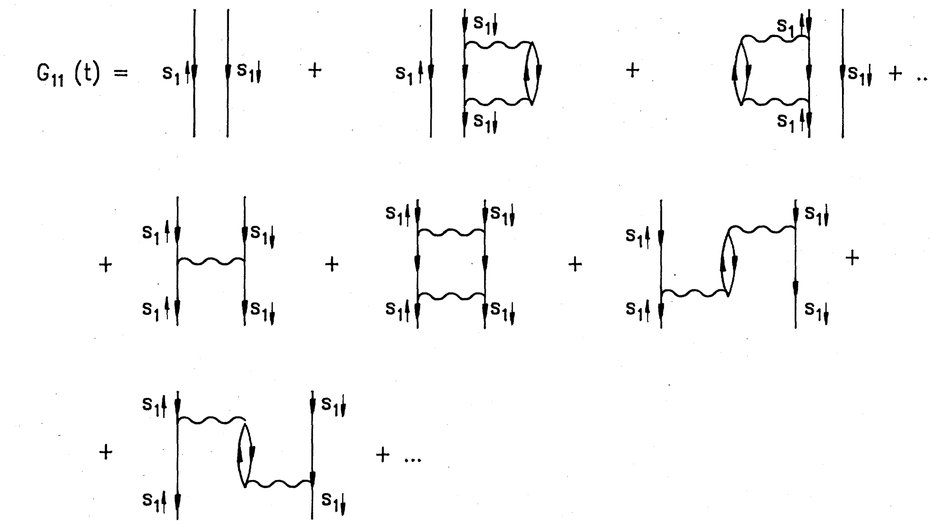

FIG. 2. The diagrams of the two-particle Green's function $\mathcal{G}_{11}(t)$ up to second order (core-valence Hamiltonian considered).

$$C(t)=\lim_{\substack{T_1\to-\infty\\ T_2\to+\infty}}[C_t(T_2,T_1)-C_0(T_2,T_1)]\,, \tag{23}$$

we readily obtain our linked-cluster theorem for the double-core-hole Green's function ($t\le 0$)

$$\mathcal{G}_{11}(t)=ie^{-i(2\varepsilon_{s_1}-V_{s_1s_1s_1s_1})t}e^{C(t)}\,. \tag{24}$$

Since the function C_0 contains all connected diagrams with wiggly interaction lines only and C_t contains all connected diagrams with wiggly interaction lines and/or interaction points (see Fig. 1), the function $C(t)$ is equal to the sum of all connected diagrams which contain *at least* one interaction point. The diagrammatic contents of this linked-cluster theorem is depicted in Fig. 3.

A major consequence of the above analysis is that the single-core-hole and double-core-hole spectra, where both vacancies are at the same atomic site, are closely related. The creation of a single core vacancy s_1^{-1} has been shown[16] to lead to the following expression for the one-particle Green's function ($t\le 0$)

$$G_{s_1\uparrow s_1\uparrow}(t)=ie^{-i\varepsilon_{s_1}t}e^{\tilde{C}(t)}\,, \tag{25a}$$

where $\tilde{C}(t)$ is defined identically to $C(t)$ except that the time-dependent interaction $V_1(t')$ in Eq. (20) is replaced by $\tilde{V}_1(t')$ which reads

$$\tilde{V}_1(t')=V_{1\uparrow}\Theta(t'-t)(\Theta-t')\,. \tag{25b}$$

The difference in the derivation of the expressions (24) and (25) is that Eq. (25) can only be derived by neglecting the spin-flip term while Eq. (24) has been derived including this term (see above). It follows that given an explicit expression for the single-core-hole spectrum, we may readily obtain the double-core-hole spectrum by simply replacing in this expression the core orbital energy and Coulomb and exchange matrix elements by new quantities according to

$$\begin{aligned}&\varepsilon_{s_1}\to 2\varepsilon_{s_1}-V_{s_1s_1s_1s_1}\,,\\ &V_{is_1\uparrow js_1\uparrow}-V_{is_1\uparrow s_1\uparrow j}\to(V_{is_1\uparrow js_1\uparrow}+V_{is_1\downarrow js_1\downarrow})\\ &\qquad\qquad-(V_{is_1\uparrow s_1\uparrow j}+V_{is_1\downarrow s_1\downarrow j})\,,\\ &V_{is_1\uparrow s_1\downarrow j}\to 0\,.\end{aligned} \tag{26}$$

This result is readily interpreted. If two core vacancies are created at the same atomic site, the valence electrons feel the *spin-free* potential of two missing charges in the core. These two charges are subject to electrostatic repulsion given by $V_{s_1s_1s_1s_1}$.

While the derivation of the double-core-hole spectrum (24) with the two vacancies at the same site is free from approximations beyond the core-valence separability, an analogous derivation for the spectrum with the vacancies at different atomic sites requires the neglect of the spin-flip term, or, more precisely, a diagonal $\overline{\mathcal{H}}$ (see Sec. III). Once $\overline{\mathcal{H}}$ is assumed diagonal, the following results are obtained ($t\le 0$):

$$\mathcal{G}_{nm}(t)=i\delta_{nm}e^{-i(\varepsilon_{s_1}+\varepsilon_{s_2}-V_{s_1s_2s_1s_2})t}e^{C_n(t)}\,,\quad n=3\text{--}6 \tag{27}$$

where $C_n(t)$ is defined identically to $C(t)$ in Eqs. (23), (20), and (22) except that the time-dependent interaction $V_1(t')$ in Eq. (20) is replaced by the appropriate interactions

$$(V_{1\downarrow}+V_{2\downarrow})\Theta(t'-t)\Theta(-t')\,,$$

$$\tfrac{1}{2}(V_{1\downarrow}+V_{1\uparrow}+V_{2\downarrow}+V_{2\uparrow})\Theta(t'-t)\Theta(-t')\,,$$

$$(V_{1\uparrow}+V_{2\uparrow})\Theta(t'-t)\Theta(-t')\,,$$

for $n=3$, 4 (5), and 6, respectively. In other words, the diagrams for the functions $\tilde{C}(t)$, $C(t)$, and $C_n(t)$, $n=3$–6, are all identical except that the meaning of the interaction point is different in each case [see, e.g., Eq.

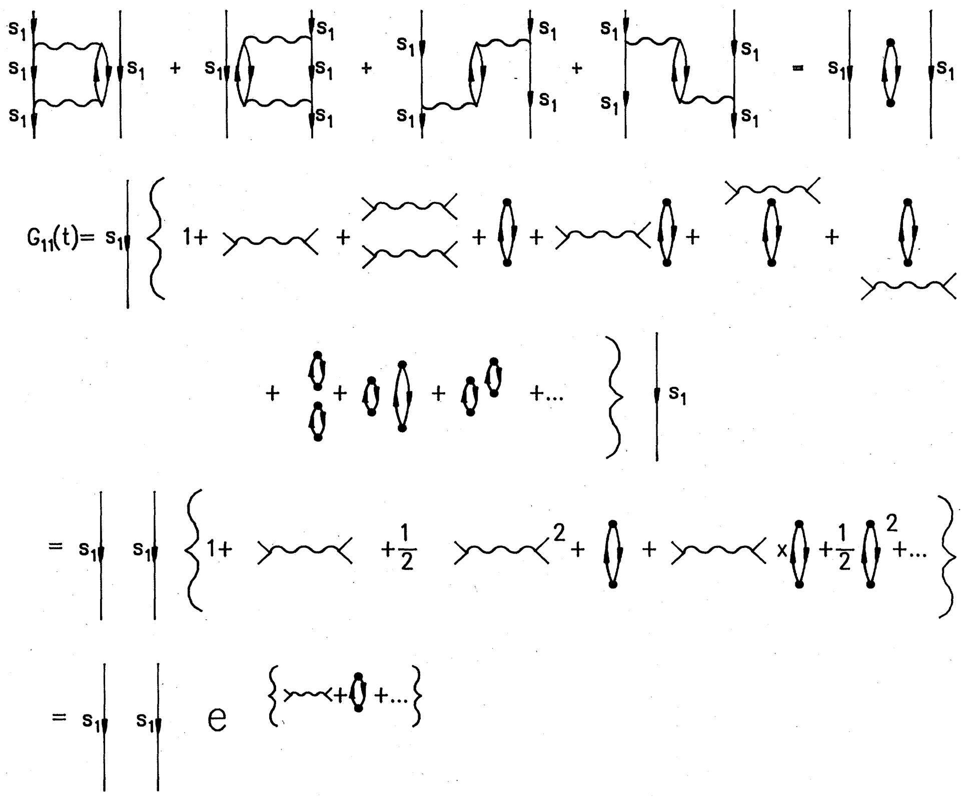

FIG. 3. On the linked-cluster theorem. Upper part: An example for the decoupling of diagrams. Lower part: The diagrammatic contents of the linked-cluster theorem.

(26) and Fig. 1].

In analogy to Eq. (26), the double-core-hole spectrum upon creation of two vacancies at different sites can be obtained from the single-core-spectrum by the substitution

$$\varepsilon_{s_1} \to \varepsilon_{s_1} + \varepsilon_{s_2} - V_{s_1 s_2 s_1 s_2},$$
$$V_{is_1\uparrow js_1\uparrow} - V_{is_1\uparrow s_1\uparrow j} \to \tfrac{1}{2}\sum_{n=1}^{2}\left[(V_{is_n\gamma js_n\gamma} + V_{is_n\gamma' js_n\gamma'}) - (V_{is_n\gamma s_n\gamma j} + V_{is_n\gamma' s_n\gamma' j})\right], \tag{28}$$

where the spin indices γ and γ' must be inserted according to the case in question. It is obvious now that analogous expressions can be obtained for the triple-, quadruple-, etc., core-hole spectra. Neglecting exchange interaction between core and valence electrons we may readily write down the general result for r core vacancies,

$$\varepsilon_{s_1} \to \sum_{n=1}^{r} \varepsilon_{s_n} - \sum_{\substack{n,m \\ (n>m)}}^{r} V_{s_n s_m s_n s_m},$$
$$V_{is_1 js_1} \to \sum_{n=1}^{r} V_{is_n js_n}, \tag{29}$$

where there is no need for spin indices and up to two of the s_n can be equal, e.g., $s_1 = s_2 \neq s_3 = s_4$.

V. SOME PROPERTIES OF THE SPECTRUM

In this section we briefly discuss the gross features of the double-core-hole spectrum in relation to the single-core-hole spectrum. It is well-known that a spectrum can be described in terms of its moments.[29] The moments M_m of a spectrum $P(\omega)$ are defined by

$$M_m = \int (\omega - E)^m P(\omega)\, d\omega, \tag{30}$$

where the parameter E may serve to simplify the calculation, since physical relevant quantities do not depend on its choice. If the spectrum $P(\omega)$ can be determined as a Fourier transform of a Green's function subject to a linked-cluster theorem as derived in Sec. IV, the moments can be related directly to the connected diagrams in the exponential. For example, for the spectrum resulting upon creation of s_1^{-2}, one obtains with the aid of Eq. (24) and the choice $E = 2\varepsilon_{s_1} - V_{s_1 s_1 s_1 s_1}$ the following relation:

$$M_m = |\tau|^2 i^m \frac{d^m}{dt^m} e^{C(t)} \Big|_{t=0}. \tag{31}$$

An equivalent, but more explicit, expression for the moments can be obtained starting from Eq. (16) for the spectra. With the choice $E = \varepsilon_{s_1}$, the moments of the single-core-hole spectrum read

$$M_m = |\tau|^2 \left\langle \psi_0^{N_v} \right| \left[E_0^{N_v} - H_v + \sum_{i,j} (V_{is_1\gamma js_1\gamma} - V_{is_1\gamma s_1\gamma j}) \times (a_i^\dagger a_j - n_i \delta_{ij}) \right]^m \left| \psi_0^{N_v} \right\rangle , \tag{32}$$

where $\gamma = \uparrow$ or $\downarrow$. In the analogous expression of Ref. 16 the term $E_0^{N_v} - H_v$ has been erroneously omitted, but this omission has no influence on the first three moments M_0, M_1, and M_2. The corresponding expressions for the moments in the various double-core-vacancy situations can be easily determined using the rules (26) and (28).

The zeroth moment M_0 gives the total intensity of the spectrum. The center of gravity of the spectrum $E_{\text{c.g.}}$ is given by $E + M_1/M_0$. Because of the Hartree-Fock potential used in this work, the first contribution to M_1 arises in third-order perturbation theory. For the single-core-hole spectrum this quantity is given by[16]

$$E_{\text{c.g.}}(s_1^{-1}) = \varepsilon_{s_1} + \Sigma_{s_1 s_1}(\infty) , \tag{33}$$

where $\Sigma_{s_1 s_1}(\infty)$ is the static part of the self-energy part,[26,30] i.e., the sum of all those diagrams of the self-energy part which are independent of energy. The center of gravity of the double-core-hole spectra $P_1(\omega)$ and $P_3(\omega)$, see Eq. (16), are now readily determined,

$$E_{\text{c.g.}}(s_1^{-2}) = 2\varepsilon_{s_1} - V_{s_1 s_1 s_1 s_1} + 2\,\Sigma_{s_1 s_1}(\infty) , \tag{34a}$$

$$E_{\text{c.g.}}(s_1^{-1} s_2^{-1}) = \varepsilon_{s_1} + \varepsilon_{s_2} - V_{s_1 s_2 s_1 s_2} + \Sigma_{s_1 s_1}(\infty) + \Sigma_{s_2 s_2}(\infty) . \tag{34b}$$

Apart from the electrostatic repulsion, the center of gravity of a double-core-hole spectrum is the sum of the centers of gravity of the corresponding single-core-hole spectra.

Equations (33) and (34) are essentially exact within the framework of core-valence separability. The spin-flip term actually not included in Eq. (32) does not affect the results for the center of gravity of the spectra. The exact moments can be obtained from the more correct expression (12) for the double-core-hole spectrum and from the corresponding expression (15) of Ref. 16 for the single-core-hole spectrum. The spin-flip term does not contribute to the ground-state expectation value of the matrix Hamiltonian $\mathscr{H}$ and thus also not to the center of gravity of the spectra. The situation is different for the second moment which depends, except in the case of the s_1^{-2} spectrum, on the spin-flip term. The contribution of this term to the spectral moments is, however, small. For the single-core-hole spectrum the contribution of this term to the second moment M_2/M_0 is

$$\langle \psi_0^{N_v} | X^\dagger X | \psi_0^{N_v} \rangle ,$$

which contains only products of exchange integrals of core and valence electrons [$X = 1/\sqrt{2}(X_+ - X_-)$, $X_\pm$ are defined in Eq. (13)].

The quantity $W = [M_2/M_0 - (M_1/M_0)^2]^{1/2}$ is a direct measure for the width of the spectrum. Neglecting terms which are products of exchange integrals, we find via Eq. (32) and the rule (26) a simple relation between the width of the double-core-hole spectrum, where both created vacancies are at the same atomic site, and that of the single-core-hole spectrum

$$W(s_1^{-2}) = 2W(s_1^{-1}) . \tag{35a}$$

It is difficult to extract from Eq. (32) and rule (28) a simple relation for the widths of the spectra in the situation where each vacancy is at a different atomic site. Because of $m = 2$ in Eq. (32) for the second moment, mixed products of Coulomb integrals belonging to different sites appear which are not present in the single-hole case. In the special situation, where both atoms are equivalent because of symmetry requirements, as is the case in, e.g., the nitrogen molecule or ethylene, we may introduce the symmetry-adapted delocalized orbitals $\phi_g = (\phi_{s_1} + \phi_{s_2})/\sqrt{2}$ and $\phi_u = (\phi_{s_1} - \phi_{s_2})/\sqrt{2}$ and use the facts that

$$V_{is_1 js_1} + V_{is_2 js_2} = V_{igjg} + V_{iuju} ,$$

$$V_{igjg} = V_{iuju} .$$

Neglecting exchange terms, one then finds

$$W(s_1^{-1} s_2^{-1}) = W(g^{-1}) + W(u^{-1}) , \tag{35b}$$

where the widths of the single-core-hole spectra of the delocalized vacancies are equal, i.e., $W(g^{-1}) = W(u^{-1})$. Interestingly, the first moment $M_1(s_1^{-1})$ is equal to $M_1(g^{-1})$ contrary to the situation found for the corresponding second moments. Neglecting again exchange terms and using $V_{is_1 js_1} - V_{is_2 js_2} = 2V_{igju}$, one obtains the following relation for these moments:

$$M_2(s_1^{-1}) = M_2(g^{-1}) + \left\langle \psi_0^{N_v} \right| \left[\sum_{i,j} V_{ig\uparrow ju\uparrow} a_i^\dagger a_j \right]^2 \left| \psi_0^{N_v} \right\rangle . \tag{35c}$$

We thus expect the widths $W(g^{-1})$ and $W(s_1^{-1} s_2^{-1})$ of the delocalized-hole and double-hole spectra to be substantially smaller than $W(s_1^{-1})$ and $W(s_1^{-2})$, respectively, for the localized-hole and double-hole spectra. The spectrum of a single delocalized hole is a hypothetical spectrum obtained by replacing s_1 in Eq. (32) for the spectral moments by the index g (or u). The spectrum following the creation of the $s_1^{-1} s_2^{-1}$ double vacancy is, on the other hand, producible in reality and exhibits all the interesting features of a delocalized-hole spectrum.

VI. SUMMARY

Making use of properties inherent to core levels, the response of the system to the creation of vacancies in the core can be evaluated. The resulting single-, double-, etc., core-hole spectrum has been expressed as the Fourier transform of the ground-state autocorrelation function of a matrix Hamiltonian which describes the motion of the valence electrons in the field of the vacancies. The dimension of the matrix Hamiltonian equals the number of possibilities to create a single-, double-, etc., vacancy. The nondiagonal elements of these Hamiltonians describe weak interactions between the various vacancy configurations, like the spin-flip of a core hole and the hopping of a core hole from one atomic site to another. The interaction involved is of the exchange type between core and valence electrons and can be neglected in many cases or subsequently taken into account by perturbation theory. Once these weak interactions are neglected, the theory is considerably simplified and a useful linked-cluster theorem is obtained. The various spectra are related to an exponential function $\exp[C(t)]$, where a diagrammatic expansion is given for $C(t)$.

It has been shown that there is an intimate relation between the single-core-hole spectrum and the double-, and multiple-core-hole spectra. Given an explicit expression for any property of a single core hole, the analogous quantity for a double or multiple core-hole can be readily determined via a simple substitution rule. This rule takes account of the nature of the vacancy. In benzene, for instance, there are four double core holes of different nature (spin symmetry not considered). The two vacancies can be located at the same atomic site or at different sites in ortho, meta, and para positions. The differences in, e.g., relaxation energies for these types of vacancies can be rationalized using the above rule.[15] From the analysis of the double-core-hole binding energies of benzene and a few other molecules it has become clear[15] that these holes probe their environment much more sensitively than single core holes. Experimental spectroscopy of double core holes could be of great interest.

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[*] Permanent address: Theoretische Chemie, Institut fuer Physikalische Chemie, Universität Heidelberg, Im Neuenheimer Feld 253, D-6900 Heidelberg, West Germany.

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