Self-consistent time-dependent Hartree–Fock calculations of dynamic polarizabilities, dispersion forces, and nuclear spin–spin coupling constants for the H_2 and HF molecules

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(Received 14 April 1975)

We present a self-consistent time-dependent Hartree–Fock scheme for calculating excitation frequencies, oscillator strengths, dynamic polarizabilities, dispersion forces, and indirect nuclear spin–spin coupling constants. *Ab initio* applications on the H_2 and HF molecules have been performed. The effect of two-particle, two-hole excitation corrections are included. The results show that the method offers an accurate and economical alternative to configuration interaction for introducing correlation in second order properties. The spin–spin coupling constants, which depend on the triplet excited states, are most influenced by the self-consistency procedure.

I. INTRODUCTION

The conventional perturbation expressions for second order electric and magnetic properties contain an infinite summation over the excited states. In the calculation of electric polarizabilities the summation runs over singlet states, whereas spin–spin coupling constants are determined from a sum over triplet states.[1] Most molecular calculations are concerned primarily with determination of ground state properties and an accurate representation of the excited states is difficult to obtain from these schemes. The time dependent Hartree–Fock (TDHF) method[2,3] or random phase approximation (RPA)[4,5] calculates directly excitation energies and oscillator strengths. Dynamic polarizabilities have previously been calculated in RPA[6] and by the similar time dependent variation–perturbation methods[7] where the excitation spectrum also is obtained directly. Recently results have been reported[8,9] where the excited states were obtained from a configuration interaction (CI) procedure. In all cases reliable numerical results have been obtained for the frequency dependent polarizability for H_2.

The present status of spin–spin coupling constant calculations is somewhat different, primarily because of the difficulties connected with representing the sum over intermediate triplet states. It is well known that the HF ground state often is triplet- (and even singlet-) unstable,[3,10] and reliable spin–spin coupling constants are thus extremely difficult to obtain in any HF-like theory including RPA and TDHF[3]. The numerical results for the HD spin–spin coupling constant, obtained on the basis of a simple HF description of triplet states, are also rather poor,[11] even in cases where the ground state is very well correlated.[12] Very extensive CI calculations with large basis sets and including all singly and doubly excited triplet configurations are now available.[13] They give, together with a many-body perturbation approach,[14] very good numerical results for HD. Considering the complexity of the above methods there still seems to be a need for a more direct way of calculating spin–spin coupling constants. The major obstacle to using TDHF schemes is that triplet excitations are poorly described. It should thus be advantageous to calculate spin–spin coupling constants in self-consistent TDHF schemes,[15,16] which are known to greatly improve the triplet spectra.[17]

We have previously proposed a self-consistent TDHF scheme based on a Green's function approach.[16,17] The equation of motion for the two-particle Green's function is decoupled in a manner consistent with the TDHF approximation. The self-consistency arises from the observation that the reduced two particle density matrix (two-matrix) is the zero-time limit of the polarization propagator[18] and that the two-matrix determines the propagator to be used in the next iteration. The poles of the propagator are the particle–hole excitation energies and the residues determine the transition moments. Like the equation-of-motion scheme,[15] the Green's function method is specifically designed to evaluate relative quantities rather than absolute energies and total wavefunctions. We shall here report calculations of oscillator strengths and excitation energies together with results for dynamic polarizabilities and spin–spin coupling constants. We will demonstrate that polarizabilities are described equally well in TDHF and self-consistent TDHF whereas results for spin–spin coupling constants, as expected, are considerably improved in the self-consistent scheme.

Besides the problem of properly including correlation, the polarizabilities and spin–spin coupling constants will of course also depend on the completeness of the basis set used. In that aspect, a Green's function approach is not different from more conventional methods. Dalgarno and Epstein[19] proved that by an appropriate choice of basis functions certain sum rules for oscillator strengths can be satisfied exactly. This criterion has been very useful in determining which basis functions to be used in calculations of dynamic polarizabilities.[8,9] No similar criterion exists for calculation of spin–spin coupling constants and the results for HD, for example, are very basis set dependent.[20] Only the most recent large scale CI calculations seem to have used basis sets which are so large that the basis set dependence is eliminated.[13]

It is our aim with the same basis set to calculate both dynamic polarizabilities and spin–spin coupling constants. It might then not be optimal to use the Dalgarno–

Epstein criterion[19] which is closely related to evaluation of polarizabilities. We will instead use as criteria on the completeness of the basis set that the TDHF oscillator strengths are the same in the dipole length and the dipole velocity formulation.[21] In other words, the disagreement between the two formulations in TDHF is used as a measure of the incompleteness of the basis set. This is not necessarily the best criterion, but it has the advantage that we choose the exponents of the atomic orbitals on the basis of which model we use rather than from consideration of which property we want to calculate. Besides the equivalance of the two formulations, we have used as an additional criterion on the completeness of the basis set the fact that the Thomas–Reiche–Kuhn sum rule must be fulfilled exactly in TDHF.[21] This procedure implies that we calculate the dynamic polarizability both in the dipole length and the dipole velocity formulation. The latter is seldom reported in the literature, and our results show that unless the basis set is very large, substantial disagreement can be found between the two, in principle, equally correct results.

We have in this paper calculated the singlet and triplet excitation spectrum together with the frequency dependent polarizability, van der Waals forces and spin–spin coupling constants for H_2 and HF. Section II briefly summarizes the self-consistent TDHF equations and Sec. III gives the formulas for the second order properties we want to calculate. The results and the discussion of those are given in the last three sections.

II. GENERAL EQUATIONS

In the Green's function formalism the TDHF equation can be derived from a moment expansion of the equation of motion for the "particle–hole" Green's function or polarization propagator. A geometric approximation to the moment expansion corresponds to what is normally called RPA or TDHF, namely the inclusion of all ring diagrams in the polarization propagator. The method has been described before,[17,22] and we will only give a brief outline of the basic concepts.

Since ring diagrams describe repeated particle–hole scattering events the basic quantities in a TDHF scheme are the particle–hole operators:

$$q_n^\dagger = a_k^\dagger a_l \,. \tag{1}$$

They are quasiboson operators which applied to the quasivacuum, assumed to be a singlet state,[16] will give an excited state if state l is occupied and state k is unoccupied in the HF ground state. The matrix representation of the Green's function that describes the propagation of a particle–hole excitation is, in the energy representation, defined as[18]

$$P_{nm}(E) = \langle\langle q_n;\ q_m^\dagger \rangle\rangle_E = \sum_p \left\{ \frac{\langle 0 | q_n | p\rangle \langle p | q_m^\dagger | 0\rangle}{E - E_p + E_0} - \frac{\langle 0 | q_m^\dagger | p\rangle \langle p | q_n | 0\rangle}{E + E_p - E_0} \right\}. \tag{2}$$

Equation (2) shows that the poles for the polarization propagator are the excitation energies and that the corresponding residues determine the transition moments. The propagator matrix will be of the dimension $2NM$, where N are the number of occupied and M the number of unoccupied spin orbitals in the ground state. The factor 2 arises since we consider both de-excitation q_n and excitation $q_n^\dagger$ operators. Let $\mathbf{q}$ be the column vector consisting of all particle–hole annihilators, i.e., of dimension NM. We will now assume that the moment expansion for the polarization propagator is geometric. The propagator in TDHF then becomes

$$\mathbf{P}(E) = \begin{Bmatrix} \langle\langle \mathbf{q};\ \mathbf{q}^\dagger \rangle\rangle_E & \langle\langle \mathbf{q};\ \mathbf{q} \rangle\rangle_E \\ \langle\langle \mathbf{q}^\dagger;\ \mathbf{q}^\dagger \rangle\rangle_E & \langle\langle \mathbf{q}^\dagger;\ \mathbf{q} \rangle\rangle_E \end{Bmatrix} = \begin{Bmatrix} \lambda & 0 \\ 0 & -\lambda \end{Bmatrix} \begin{Bmatrix} E\lambda - \mathbf{A} & -\mathbf{B} \\ -\mathbf{B} & -E\lambda - \mathbf{A} \end{Bmatrix}^{-1} \begin{Bmatrix} \lambda & 0 \\ 0 & -\lambda \end{Bmatrix}. \tag{3}$$

The λ matrix, which defines the metric, is in a natural orbital[23] basis diagonal with occupation number differences in the diagonal

$$\langle [q_m,\ q_{m'}^\dagger] \rangle = \delta_{mm'} \langle n_l - n_k \rangle = \delta_{mm'} \lambda_m \,. \tag{4}$$

The matrices $\mathbf{A}$ and $\mathbf{B}$ are the second moments in the moment expansion of Eq. (2):

$$A_{mm'} = \langle [[q_m,\ H],\ q_{m'}^\dagger] \rangle \tag{5}$$

$$B_{mm'} = \langle [[q_m,\ H],\ q_{m'}] \rangle \,. \tag{6}$$

All average values are taken over the quasivacuum and H is the Hamiltonian of the system. It is seen from Eq. (3) that the determination of the poles for $\mathbf{P}(E)$ corresponds to solving a non-Hermitian eigenvalue problem. By means of a series of transformations,[3] it is possible to express $\mathbf{P}(E)$ in a form which directly yields excitation energies and which only requires a solution of two Hermitian eigenvalue problems for $\mathbf{A}+\mathbf{B}$ and $\mathbf{A}-\mathbf{B}$:

$$\mathbf{P}(E) = \begin{Bmatrix} \lambda^{1/2} & 0 \\ 0 & \lambda^{1/2} \end{Bmatrix} \begin{Bmatrix} \mathbf{Z} & \mathbf{Y} \\ \mathbf{Y} & \mathbf{Z} \end{Bmatrix} \begin{Bmatrix} (E\mathbf{1} - \omega)^{-1} & 0 \\ 0 & -(E\mathbf{1} + \omega)^{-1} \end{Bmatrix} \times \begin{Bmatrix} \mathbf{Z}^\dagger & \mathbf{Y}^\dagger \\ \mathbf{Y}^\dagger & \mathbf{Z}^\dagger \end{Bmatrix} \begin{Bmatrix} \lambda^{1/2} & 0 \\ 0 & \lambda^{1/2} \end{Bmatrix}. \tag{7}$$

The exact definition of $\mathbf{Z}$, $\mathbf{Y}$ and ω in terms of $\mathbf{A}$ and $\mathbf{B}$ can be found elsewhere.[24]

It is well known that the zero-time limit of a matrix representation of the double-time two-particle Green's function gives the two-matrix.[18] The double-time Green's function is the Fourier transform of Eq. (2). The integration over E can be transformed into a contour integral in the complex E-plane and gives the following for the two-matrix:

$$M_{m'm} = \langle q_m q_{m'}^\dagger \rangle = \text{Residues of } \langle\langle q_m;\ q_{m'}^\dagger \rangle\rangle_{E>0} \,. \tag{8}$$

The two-matrix in TDHF can now easily be found from Eq. (7):

$$\mathbf{M} = \begin{Bmatrix} \langle \mathbf{q}\mathbf{q}^\dagger \rangle & \langle \mathbf{q}\,\mathbf{q} \rangle \\ \langle \mathbf{q}^\dagger \mathbf{q}^\dagger \rangle & \langle \mathbf{q}^\dagger \mathbf{q} \rangle \end{Bmatrix} = \begin{Bmatrix} \lambda^{1/2} & 0 \\ 0 & \lambda^{1/2} \end{Bmatrix} \begin{Bmatrix} \mathbf{Z}\mathbf{Z}^\dagger & \mathbf{Y}\mathbf{Z}^\dagger \\ \mathbf{Z}\mathbf{Y}^\dagger & \mathbf{Y}\mathbf{Y}^\dagger \end{Bmatrix} \begin{Bmatrix} \lambda^{1/2} & 0 \\ 0 & \lambda^{1/2} \end{Bmatrix}. \tag{9}$$

In TDHF the HF ground state is used in the evaluation of $\mathbf{A}$ and $\mathbf{B}$ from Eqs. (5) and (6). This enables us to

write down closed expressions for $A_{mm'}$ and $B_{mm'}$ in the molecular orbital (MO) basis.[3] In this case $\boldsymbol{\lambda}$ is a unit matrix and Eq. (7) directly determines the excitation energies and oscillator strengths. From Eq. (9) we can determine a new two-matrix and Eqs. (5) and (6) determine other **A** and **B** matrices. This procedure defines what we have called the self-consistent polarization propagator approximation (SPPA), since the iterative scheme is continued until we have obtained a self-consistent solution for $\mathbf{P}(E)$. The TDHF approximation is inconsistent from the point of view that the HF ground state is not the vacuum for TDHF excitation. When self-consistency is reached the ground state becomes the SPPA quasivacuum. Since we are iterating on the two-electron densities we can, however, not determine the quasivacuum, and we do not know whether or not the two-matrix is N-representable.[25] We have examined this problem by calculating certain sum rules and internal constraints that an N-representable two-matrix must fulfill.[24] In the present application, as well as earlier,[17] we have found that according to those criteria the two-matrix was nearly N-representable. Especially for the self-consistent solution the calculated sums deviated very little from the exact results.

As stated previously, **A** and B are square matrices of dimension NM. By introducing the triplet and singlet particle-hole tensor operators,

$$\begin{aligned}
&S=1,\ M_s=1 \ : \ {}^3Q^1_{lk} = -a^\dagger_{l\alpha}a_{k\beta}\\
&\quad ,\ M_s=0 \ : \ {}^3Q^o_{lk} = \{a^\dagger_{l\alpha}a_{k\alpha} - a^\dagger_{l\beta}a_{k\beta}\}/\sqrt{2}\\
&\quad ,\ M_s=-1 : \ {}^3Q^{-1}_{lk} = a^\dagger_{l\beta}a_{k\alpha}\\
&S=0,\ M_s=0 \ : \ {}^1Q_{lk} = \{a^\dagger_{l\alpha}a_{k\alpha} + a^\dagger_{l\beta}a_{k\beta}\}/\sqrt{2}
\end{aligned} \tag{10}$$

the matrix problem will separate into a singlet and triplet problem each of dimension $NM/4$. This does not mean that the singlet and triplet problems are independent. For example, the calculation of **A** in the triplet manifold does require knowledge of the singlet two-matrix. This type of coupling will also be present when molecular symmetry is used to further reduce the size of the matrix problem.

In our previous applications of SPPA to π-electron systems we have calculated **A** and **B** in the atomic representation[17] and we had to transform the **A** and **B** matrices into the MO representation. It is advantageous to calculate **A** and **B** directly in the representation in which we know **M**, i.e., the MO representation. In this representation the TDHF matrix elements are

$$\begin{aligned}
{}^1A^{(0)}_{kl,k'l'} &= \delta_{kk'}\delta_{ll'}(\epsilon_k - \epsilon_l) - (kk'|l'l) + 2(kl|l'k')\\
{}^1B^{(0)}_{kl,k'l'} &= (kl'|k'l) - 2(kl|k'l')\\
{}^3A^{(0)}_{kl,k'l'} &= \delta_{kk'}\delta_{ll'}(\epsilon_k - \epsilon_l) - (kk'|l'l)\\
{}^3B^{(0)}_{kl,k'l'} &= (kl'|k'l),
\end{aligned} \tag{11}$$

where

$$(kk'|l'l) = \int u^*_k(1)\,u_{k'}(1)\,r^{-1}_{12}\,u^*_{l'}(2)\,u_l(2)\,d\tau_1\,d\tau_2 . \tag{12}$$

We have used the notation that kk' (ll') are states which are unoccupied (occupied) in the MO ground state.

Notice that TDHF reduces to the monoexcited CI (MECI) approximation when $\mathbf{B}=\mathbf{0}$, since the excitation energies are then determined from a diagonalization of the **A** matrix alone. Furthermore, if we only consider the diagonal elements of **A**, we find excitation energies as given in the HF approximation. We thus have a series of approximations HF → MECI → TDHF → SPPA, which can be studied and compared.

Because the metric $\boldsymbol{\lambda}$ does not change during the iterations,[17] the indexing which refers to states which are occupied or unoccupied in the MO ground state can be kept in SPPA. Going beyond TDHF, the quasivacuum changes and the two-matrix will not, as in HF, merely have elements which are integers and zeros. The electronic Hamiltonian in second quantization can be written as[18]

$$H = \sum_{rs} h_{rs}a^\dagger_r a_s + \frac{1}{2}\sum (rs\,|\,r's')\,a^\dagger_r a^\dagger_{r'}a_{s'}a_s , \tag{13}$$

and general formulas for matrix elements of **A** and **B** can be obtained from Eqs. (5) and (6):

$${}^1A_{kl,k'l'} = {}^1A^{(0)}_{kl,k'l'} + \tfrac{1}{2}\delta_{ll'}\sum_{rs}^{occ}\sum_{t}^{unocc}(kr|ts)\{\langle {}^1Q_{k's}\,{}^1Q_{tr}\rangle + 3\langle {}^3Q_{k's}\,{}^3Q_{tr}\rangle\} + \tfrac{1}{2}\delta_{kk'}\sum_{rs}^{unocc}\sum_{t}^{occ}(rl\,|\,st)\{\langle {}^1Q_{rt}\,{}^1Q_{st'}\rangle + 3\langle {}^3Q_{rt}\,{}^3Q_{st'}\rangle\} \tag{14}$$

$$\begin{aligned}
{}^1B_{kl,k'l'} = {}^1B^{(0)}_{kl,k'l'} &- \sum_{rs}^{occ}(sl'|rl)\langle {}^1Q_{rk}\,{}^1Q_{sk'}\rangle - \sum_{rs}^{unocc}(kr|k's)\langle {}^1Q_{l's}\,{}^1Q_{lr}\rangle + \sum_{s}^{unocc}\sum_{r}^{occ}(ks\,|\,rl')\,\langle {}^1Q_{ls}\,{}^1Q_{rk'}\rangle + \sum_{s}^{occ}\sum_{r}^{unocc}(k'r\,|\,sl)\\
&\times\langle {}^1Q_{l'r}\,{}^1Q_{sk}\rangle - \frac{1}{2}\sum_{s}^{unocc}\sum_{r}^{occ}(kl'|rs)\{\langle {}^1Q_{ls}\,{}^1Q_{rk'}\rangle + 3\langle {}^3Q_{ls}\,{}^3Q_{rk'}\rangle\} - \frac{1}{2}\sum_{s}^{occ}\sum_{r}^{unocc}(k'l\,|\,sr)\{\langle {}^1Q_{l'r}\,{}^1Q_{sk}\rangle + 3\langle {}^3Q_{l'r}\,{}^3Q_{sk}\rangle\} .
\end{aligned} \tag{15}$$

The SPPA corrections to $^3\mathbf{A}$ are the same as to $^1\mathbf{A}$, and the corrections to $^3\mathbf{B}$ are as to $^1\mathbf{B}$ except that the singlet two-electron densities in the first four terms must be replaced by triplet elements. In the derivations of the expressions for **A** and **B** we have used

$$\langle a^\dagger_k a_l a^\dagger_{l'} a_{k'}\rangle = 0, \tag{16}$$

which is consistent with the MO picture that is retained throughout the iterative scheme. The only non-vanishing elements of the two-matrix involving particle–hole operators are hence of the type

$$\langle a^\dagger_k a_l a^\dagger_{k'} a_{l'}\rangle \neq 0 . \tag{17}$$

As mentioned earlier, the elements of an N-representable two-matrix should fulfill certain constraints and sum rules. This means that it is possible to get

TABLE I. Vertical excitation energies, ω_{on} (in eV), and oscillator strengths in the dipole length, f_L, and the dipole velocity formulation, f_V, calculated for H_2 ($R = 1.40$ bohr) in mono-excited CI (MECI), TDHF, SPPA, and SPPA with $2p-2h$ corrections ($2p-2h$). All excitations are from the $X\,^1\Sigma_g^+$ ground state.

Final state[a]		$B\,^1\Sigma_u^+$	$E,F\,^1\Sigma_g^+$	$B'\,^1\Sigma_u^+$	$^1\Sigma_u^+$	$^1\Sigma_u^+$	$C\,^1\Pi_u$	$^1\Pi_u$	$^1\Pi_u$	$b\,^3\Sigma_u^+$	$a\,^3\Sigma_g^+$	$^3\Sigma^+$	$c\,^3\Pi_u$
MECI	ω_{on}	12.74	13.08	14.65	15.95	20.49	13.12	14.78	23.56	9.99	12.07	14.17	12.38
	f_L	0.308	0.0	0.052	0.086	0.276	0.171	0.047	0.528				
	f_V	0.228	0.0	0.050	0.065	0.162	0.138	0.040	0.411				
TDHF	ω_{on}	12.67	13.06	14.63	15.92	20.35	13.11	14.77	23.46	9.55	12.01	14.14	12.34
	f_L	0.285	0.0	0.044	0.069	0.210	0.162	0.043	0.463				
	f_V	0.288	0.0	0.061	0.074	0.189	0.156	0.045	0.457				
SPPA	ω_{on}	13.60	13.95	15.52	16.82	21.34	13.99	15.65	24.43	10.92	12.94	15.04	13.25
	f_L	0.296	0.0	0.047	0.077	0.230	0.173	0.046	0.491				
	f_V	0.253	0.0	0.056	0.073	0.188	0.141	0.042	0.436				
$2p-2h$	ω_{on}	13.06	13.47	15.08	16.38	20.90	13.54	15.23	24.14	10.70	12.66	14.65	12.94
	f_L	0.297	0.0	0.043	0.068	0.213	0.169	0.043	0.482				
	f_V	0.285	0.0	0.057	0.069	0.187	0.149	0.042	0.441				
RPA[b]	ω_{on}	12.66		14.59	15.67		13.08	14.76					
	f_L	0.293		0.062	0.077		0.165	0.041					
'Exact'	ω_{on}[c]	12.75	13.13*	14.85[f]			13.29*			10.65	12.54		13.37[d]
	f_L[e]	0.300	0.0	0.057[f]			0.178*						
	f_V[e]	0.307	0.0										

[a] An assignment was only possible for some of the calculated excitation energies.
[b] Martin *et al.*, from Ref. 36.
[c] Calculated from potential energy curves given by W. Kolos and L. Wolniewicz, J. Chem. Phys. **43**, 2429 (1965); **48**, 3672 (1968); **50**, 3228 (1969). An asterisk indicates that the number was estimated by interpolation.
[d] J. C. Browne, J. Chem. Phys. **40**, 43 (1964).
[e] L. Wolniewicz, J. Chem. Phys. **51**, 500 (1969).
[f] L. Wolniewicz, Chem. Phys. Lett. **31**, 248 (1975).

other (in principle, equivalent) expressions for **A** and **B**. None of the two-matrices used to compute **A** and **B** are exactly N-representable. Especially the triplet two-matrix in TDHF is far from satisfying any sum rules. Since these elements are used in the construction of **A** and **B** from Eqs. (14) and (15) the first iteration can sometimes be so incorrect that we get convergence problems in the iterative scheme. The singlet two-matrix is, even in the first iteration, nearly N-representable. Therefore we used the formal identity

$$\langle {}^3Q_{rs}\,{}^3Q_{tv}\rangle = -\tfrac{1}{3}\{\langle {}^1Q_{rs}\,{}^1Q_{tv}\rangle + 2\langle {}^1Q_{rv}\,{}^1Q_{ts}\rangle\} \tag{18}$$

to express **A** and **B** in terms of singlet two-electron densities alone. The iterative scheme becomes with this redefinition numerically more stable and the computational effort is also greatly reduced since iteration need only be done then in the singlet case.

It has been found in the equation-of-motion method that it is often necessary to go beyond self-consistent RPA treatments when describing singlet excitation spectra.[26] We have experienced the same trend, namely that SPPA often gives singlet excitation energies which are too large.[17] This is probably due to an undercorrelation of excited states as compared to the ground state. One way to improve self-consistent RPA schemes would be to try to include two-particle, two-hole excitations ($2p-2h$). Shibuya *et al.*[27] proposed a first order perturbation treatment of the $2p-2h$ corrections. We have found that to a very good approximation the $2p-2h$ corrections can be represented by a perturbation having the TDHF form in Eq. (3).[28] If we define

$$\mathbf{A}_{\mathrm{I}} = \tfrac{1}{2}\{\langle [[\mathbf{q}, H], \mathbf{q}^\dagger\mathbf{q}^\dagger]\rangle + \langle [\mathbf{q}, [H, \mathbf{q}^\dagger\mathbf{q}^\dagger]]\rangle\} \tag{19}$$

$$\mathbf{A}_{\mathrm{II}} = \tfrac{1}{2}\{\langle [[\mathbf{q}\mathbf{q}, H], \mathbf{q}^\dagger\mathbf{q}^\dagger]\rangle + \langle [\mathbf{q}\mathbf{q}, [H, \mathbf{q}^\dagger\mathbf{q}^\dagger]]\rangle\} \tag{20}$$

we find approximatively that

$$\delta\mathbf{A} = \mathbf{A}_{\mathrm{I}}^\dagger \mathbf{A}_{\mathrm{II}}^{-1} \mathbf{A}_{\mathrm{I}} \tag{21}$$

$$\delta\mathbf{B} = 0, \tag{22}$$

where $\delta\mathbf{A}$ and $\delta\mathbf{B}$ are the $2p-2h$ corrections to **A** and **B** defined in Eqs. (5) and (6). The derivation can be found elsewhere.[28] Since $\delta\mathbf{A}$ is only a small correction to **A** we have iterated the SPPA equations to self-consistency

TABLE II. The basis functions $\Phi_{n\ell m}(r,\theta,\varphi) = N_n r^{n-1} e^{-\zeta r} Y_{\ell m}(\theta,\varphi)$, used in the calculations of second order properties and excitation spectrum for H_2.

n	ℓ	m	ζ
1	0	0	1.33
1	0	0	2.47
2	0	0	0.9
3	0	0	0.7
4	0	0	0.2
2	1	0	0.8
2	1	0	0.2
2	1	1	1.15
2	1	−1	1.15
3	1	0	0.5
3	1	1	0.6
3	1	−1	0.6
3	1	1	0.3
3	1	−1	0.3

TABLE III. Energy weighted sum rules for H_2 ($R = 1.40$ bohr) in mono-excited CI, (MECI), TDHF, SPPA, and SPPA corrected with $2p-2h$ excitations ($2p-2h$). Results are given in the dipole length (L) and the dipole velocity (V) formulation. Atomic units are used.

		MECI	TDHF	SPPA	$2p-2h$	RPA[a]	VD[b]	Other
$S_\parallel(2)$	L	204	1.84	2.05	1.98	1.64	0.82	
	V	0.88	1.01	1.07	1.05			
$S_\perp(2)$	L	1.35	1.18	1.37	1.30	2.85	1.93	
	V	1.06	1.17	1.21	1.19			
$S_\parallel(1)$	L	1.76	1.41	1.57	1.47	1.33	1.21	
	V	1.06	1.26	1.27	1.28			
$S_\perp(1)$	L	1.69	1.50	1.67	1.61	1.84	1.67	
	V	1.33	1.48	1.46	1.47			
$S_\parallel(0)$	L	2.44	2.00	2.13	2.04	1.99	2.00	2[c]
	V	1.65	2.00	1.87	1.96			2[c]
$S_\perp(0)$	L	2.24	2.00	2.13	2.08	2.00	2.00	2[c]
	V	1.77	1.97	1.86	1.90			2[c]
$S_\parallel(-1)$	L	4.00	3.40	3.40	3.38	3.48	3.58	3.45[d]
	V	2.86	3.51	3.05	3.33			
$S_\perp(-1)$	L	3.15	2.86	2.89	2.88	2.84	2.91	2.83[d]
	V	2.51	2.81	2.50	2.61			
$S_\parallel(-2)$	L	7.14	6.25	5.82	6.04	6.48	6.80	6.38[e]
	V	5.26	6.51	5.25	6.01			
$S_\perp(-2)$	L	4.79	4.40	4.21	4.31	4.61	4.77	4.58[e]
	V	3.83	4.32	3.60	3.89			

[a] Martin *et al.* in Ref. 6.
[b] Semiempirical results of Ref. 31.
[c] Exact value.
[d] W. Kolos and L. Wolniewicz, J. Chem. Phys. 41, 3663 (1964).
[e] W. Kolos and L. Wolniewicz, J. Chem. Phys. 46, 1426 (1967).

as described above, and then added the $2p-2h$ correction to the self-consistent result. This means that the $2p-2h$ correction is not calculated with respect to the SPPA quasivacuum; however, because of the smallness of the corrections, this is only a slight inconsistency in the treatment.

III. CALCULATION OF PROPERTIES

An advantage of Green's function theory is that many molecular properties can easily be derived from the propagator. The two-particle propagator is a convenient starting point for determination of excitation energies and oscillator strengths as well as molecular properties such as dispersion forces and spin–spin coupling constants.[29] Equation (7) directly gives the excitation energies ($\pm\omega$) and a comparison of Eqs. (2) and (7) shows

TABLE IV. Energy weighted sum rules, the lowest excitation energies (in eV) and corresponding oscillator strengths, f, for H_2. Results are given in TDHF using the basis set of Ref. 35.

	Dipole length	Dipole velocity
$S_\parallel(0)$	2.04	1.97
$S_\perp(0)$	2.71	1.55
$S_\parallel(-1)$	3.49	3.39
$S_\perp(-1)$	3.73	1.80
$f(\sigma-\sigma^*)$	0.603(14.45[a])	0.563(14.45[a])
$f(\sigma-\pi^*)$	0.902(31.12[a])	0.515(31.12[a])

[a] Excitation energies.

TABLE V. Transition moments for the two lowest allowed σ transitions for H_2 (columns 1 and 3 in Table I), given in the dipole length (L) and the dipole velocity (V) formulation.

		$B\,^1\Sigma_u^+$	$B\,^1\Sigma_u^+$
MECI	L	0.994	0.382
	V	0.400	0.201
TDHF	L	0.959	0.351
	V	0.448	0.222
SPPA	L	0.942	0.353
	V	0.435	0.219
$2p-2h$	L	0.964	0.340
	V	0.452	0.218

that

$$\langle 0 \mid q_n \mid p\rangle = \lambda_n^{1/2} Z_{np} \tag{23}$$

$$\langle 0 \mid q_m^\dagger \mid p\rangle = \lambda_m^{1/2} Y_{mp}\,, \tag{24}$$

where $|0\rangle$ is the quasivacuum and $|p\rangle$ an excited state. Those relations can be used to determine transition moments. For a general Hermitian one-electron operator $\hat{\mathbf{M}}$ the transition moment is

$$\langle 0 \mid \hat{\mathbf{M}} \mid p\rangle = \sum_{k>l} \{M_{kl}\langle 0 \mid a_k^\dagger a_l \mid p\rangle + M_{kl}^*\langle 0 \mid a_l^\dagger a_k \mid p\rangle\}$$

$$= \sum_{n=(kl)} \lambda_n^{1/2}\{M_n^* Z_{np} + M_n Y_{np}\} \tag{25}$$

where

$$M_n = M_{kl} = \int u_k^* \hat{\mathbf{M}} u_l \, d\tau,$$

and u_k is an MO.

If we substitute for $\hat{\mathbf{M}}$ the operators $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$, we get, using $\mathbf{Y}$, $\mathbf{Z}$ and the matrix elements of $\hat{\mathbf{r}}$ and $\hat{\mathbf{p}}$ in the MO basis, the transition moments in the dipole length and dipole velocity formulation respectively. The corresponding oscillator strengths can be found as (in a.u.)

$$f_{op}^L = \tfrac{2}{3}\left|\langle 0 \mid \hat{\mathbf{r}} \mid p\rangle\right|^2 \omega_{op} \tag{26}$$

$$f_{op}^V = \tfrac{2}{3}\left|\langle 0 \mid \hat{\mathbf{p}} \mid p\rangle\right|^2 / \omega_{op}\,. \tag{27}$$

Harris[21] has shown that TDHF gives identical oscillator strengths in the dipole length and velocity formulation. Disagreement is due to the incompleteness of the basis set used. The equivalence (in TDHF only) has been used as a criterion on the completeness of the basis set. We have examined individual oscillator strengths as well as a few energy weighted sum rules of the type

$$S(n) = \sum_p f_{op}\omega_{op}^n\,, \tag{28}$$

where f_{op} can be either of the two equivalent oscillator strengths. For $n = 0$ the Thomas–Reiche–Kuhn sum rule states that

$$S(0) = N, \tag{29}$$

where N is the number of electrons in the system. This sum rule is fulfilled exactly in TDHF.[21] For a diatomic molecule it is often convenient to distinguish between transitions along the internuclear axis ($\parallel$) and perpendic-

TABLE VI. Static dipole polarizability and anisotropy for H_2 at $R=1.40$ bohr. Results are given in HF, MECI (mono-excited CI), TDHF, SPPA, and SPPA corrected with $2p-2h$ excitations ($2p-2h$). No vibrational averaging is included.

	$\alpha_\parallel(a_0^3)$		$\alpha_\perp(a_0^3)$		$\alpha\ (a_0^3)$		$\gamma\ (a_0^3)$	
	Length	Velocity	Length	Velocity	Length	Velocity	Length	Velocity
HF	6.29	3.59	4.44	3.01	5.06	3.21	1.85	0.58
MECI	7.14	5.26	4.79	3.83	5.57	4.31	2.35	1.43
TDHF	6.25	6.51	4.40	4.32	5.02	5.05	1.85	2.20
SPPA	5.82	5.25	4.21	3.60	4.74	4.15	1.61	1.65
$2p-2h$	6.04	6.01	4.31	3.89	4.88	4.60	1.73	2.13
FBI[a]	6.41		4.57		5.18		1.84	
KW[b]	6.38		4.58		5.18		1.80	
FBII[a]	6.74		4.74		5.41		2.01	
Experiment[d]					5.44			

[a]Reference 9, without vibrational and rotational averaging.
[b]W. Kolos and L. Wolniewicz, J. Chem. Phys. 46, 1426 (1967).
[c]Reference 9. Results include vibrational and rotational averaging.
[d]D. M. Golden and B. Crawford, Jr., J. Chem. Phys. 36, 1654 (1962).

ular to the axis ($\perp$).[30] We know that

$$S_\parallel(0)=N \tag{30}$$

$$S_\perp(0)=N, \tag{31}$$

where we in general have defined

$$S_\parallel(n)=3\sum_p f_{op}(z)\,\omega_{op}^n \tag{32}$$

$$S_\perp(n)=\frac{3}{2}\sum_p f_{op}(x,y)\,\omega_{op}^n \tag{33}$$

and

$$S(n)=\tfrac{1}{3}\{S_\parallel(n)+2S_\perp(n)\}. \tag{34}$$

$f_{op}(z)$ is the oscillator strength for transitions polarized along the internuclear axis (σ-transitions) and $f_{op}(x,y)$ is the sum of oscillator strengths for transitions with polarization directions perpendicular to the internuclear axis (non σ-transitions). All the sum rules give, as stated above, identical TDHF-results in the dipole length and dipole velocity approximation.

Knowing the oscillator strengths, it is straightforward to calculate the frequency dependent dynamic dipole polarizability tensor for a diatomic molecule[30]:

$$\alpha_\parallel(\omega)=3\sum_{p\neq 0} f_{op}(z)/(\omega_{op}^2-\omega^2) \tag{35}$$

$$\alpha_\perp(\omega)=\frac{3}{2}\sum_{p\neq 0} f_{op}(x,y)/(\omega_{op}^2-\omega^2) \tag{36}$$

The trace of the polarizability tensor is

$$\alpha(\omega)=\tfrac{1}{3}[\alpha_\parallel(\omega)+2\alpha_\perp(\omega)] \tag{37}$$

and the anisotropy is

$$\gamma(\omega)=\alpha_\parallel(\omega)-\alpha_\perp(\omega). \tag{38}$$

Several macroscopic properties such as the refractive index, the Verdet constant, and Rayleigh scattering cross section are directly related to $\alpha(\omega)$ and $\gamma(\omega)$.[6,31] The second-order dipole–dipole dispersion energy for diatomic molecules is also easily determined from knowledge of $\alpha_\parallel(\omega)$.[30] Evaluation of the basic quantities in Eqs. (35) and (36) involves an infinite summation. In TDHF[6] and SPPA we perform the summation directly over the calculated excited states and thus approximately represent the continuum with a finite number of discrete levels, as done successfully in many previous calculations.

It is well-known that TDHF often gives very incorrect triplet excitation energies and sometimes even shows that the ground state is triplet-unstable.[3,10] The self-consistent TDHF scheme has been shown[15,17] to greatly improve the description of the triplet spectrum. The indirect nuclear spin–spin coupling constant can be expressed as an infinite sum over triplet excited states.[1] It is reasonable to assume that SPPA should be able to give a more reliable determination of spin–spin coupling constants than for example HF-like theories. Ramsey[32] has shown that for small molecules the most important contribution to the indirect spin–spin coupling between nuclei comes from the contact interaction. Usually the interaction energy is expressed as

$$\Delta E_{ss}=\sum_{NN'} \mathbf{I}_N\,\mathbf{J}_{NN'}\,\mathbf{I}_N \tag{39}$$

where $\mathbf{I}_N=(I_{Nx}, I_{Ny}, I_{Nz})$ is the nuclear spin. $\mathbf{J}_{NN'}$ is the spin–spin coupling tensor. According to Ramsey,[32]

TABLE VII. Dispersion-force coefficients[a] for a pair of hydrogen molecules with $R=1.40\ a_0$. Atomic units.

	C		Γ		Δ	
	Length	Velocity	Length	Velocity	Length	Velocity
HF	12.65	5.16	0.104	0.038	0.011	0.002
MECI	13.80	8.18	0.113	0.080	0.014	0.007
TDHF	11.01	11.10	0.093	0.113	0.010	0.014
SPPA	10.51	8.07	0.086	0.103	0.008	0.012
$2p-2h$	10.76	9.49	0.088	0.122	0.009	0.016
LGK[b]	11.5		0.097		0.010	
FB[c]	11.35		0.099		0.010	

[a]For a definition of C, Γ, and Δ see Ref. 30.
[b]Reference 30.
[c]Reference 9.

$$\Delta E_{ss} = \sum_{NN'} \sum_{p\neq 0} \frac{\langle 0|H_F(N)|p\rangle\langle p|H_F(N')|0\rangle + \langle 0|H_F(N')|p\rangle\langle p|H_F(N)|0\rangle}{E_0 - E_p}, \tag{40}$$

where $H_F(N)$ is the contact Hamiltonian which in second quantization can be expressed as[33]

$$H_F(N) = \sum_{rt} q^N_{rt} \{ {}^3_1Q_{rt}(I_{Nx} - iI_{Ny}) + {}^3_{-1}Q_{rt}(I_{Nx} + iI_{Ny}) + \sqrt{2}\ {}^3_0Q_{rt} I_{Nz} \} \tag{41}$$

with

$$q^N_{rt} = \frac{4\pi}{3} g\beta\hbar\gamma_N u^*_r(\mathbf{R}_N) u_t(\mathbf{R}_N) . \tag{42}$$

g is the electronic electromagnetic ratio, β the Bohr magneton, γ_N the nuclear gyromagnetic factor for nucleus N with position $\mathbf{R}_N$. The field operator is expanded in a complete set $\{u_r\}$ which we will approximate with the MO's of the system. The particle–hole operators are defined in Eq. (10). Comparison of Eqs. (2), (40), (41) and (42) shows that

$$\Delta E_{ss} = \sum_{NN'} Re\langle\langle H_F(N);\ H_F(N')\rangle\rangle_{E=0}$$

$$= 2 \sum_{NN'} \sum_{rt} \sum_{r't'} q^N_{rt} q^{N'}_{r't'} Re\langle\langle {}^3Q_{rt};\ {}^3Q_{r't'}\rangle\rangle_{E=0} I_N \cdot I_{N'} . \tag{43}$$

Equation (39) hence defines

$$\mathbf{J}_{NN'} = 2 \sum_{rt} \sum_{r't'} q^N_{rt} q^{N'}_{r't'} Re\langle\langle {}^3Q_{rt};\ {}^3Q_{r't'}\rangle\rangle_{E=0} \mathbf{I} , \tag{44}$$

where $\mathbf{I}$ is a unit dyadic.

The spin–spin coupling constant measured in nonviscous high resolution NMR experiments is the isotropic part of $\mathbf{J}_{NN'}$,[34] i.e.,

$$J_{NN'} = 2 \sum_{rt} \sum_{r't'} q^N_{rt} q^{N'}_{r't'} Re\langle\langle {}^3Q_{rt};\ {}^3Q_{r't'}\rangle\rangle_{E=0} , \tag{45}$$

If we use the actual form of the two-particle propagator in Eq. (3) the spin–spin coupling constant can be evaluated directly, in any iteration of our scheme, as

$$J_{NN'} = -4 \sum_{ll'}^{occ} \sum_{kk'}^{unocc} \lambda_{lk} ({}^3\mathbf{A} - {}^3\mathbf{B})^{-1}_{lk,l'k'} \lambda_{l'k'} q^N_{lk} q^{N'}_{l'k'} . \tag{46}$$

This final formula shows clearly that spin–spin coupling constants depend on the triplet excited states alone.

IV. RESULTS FOR H_2

The excitation spectrum for H_2 in Table I was evaluated with the basis set given in Table II. The basis functions were chosen to minimize the difference between TDHF oscillator strengths obtained in the dipole length and the dipole velocity formulation. We have considered the equivalence of individual oscillator strengths as well as certain energy weighted sum rules, some of which are given in Table III. In variational schemes the basis functions are normally chosen to minimize the ground state energy. This gives a good description of ground state properties but does not necessarily lead to an optimal choice for excited states. The basis set of Das and Wahl[35] represents such a choice for H_2. We used this basis set, consisting of 14 optimized Slater-type orbitals (STO), to calculate the excitation spectrum for H_2. The results are given partly in Table IV and partly elsewhere.[28] Comparison between the results in Tables I and IV clearly shows that basis set of Das and Wahl gives a rather poor description of the excitation spectrum. That this is especially true for the σ–π^* transitions is understandable since H_2 in HF only has occupied orbitals with σ symmetry.

We might get an idea of the completeness of the basis set from a comparison of our TDHF results and the RPA results of Martin *et al.*[36] The methods are the same and the deviations are caused by the different choice of basis set. Their Gaussian (GTO) basis set, being much larger than ours, gives a completely different (discrete) representation of the continuum states. Martin *et al.*[36] only report transition energies for the allowed singlet transitions. For the lowest allowed transitions we find very good agreement between TDHF and RPA results of Ref. 36 and Table III shows that the overall quality of the sum rules obtained with 54 GTO's and 28 STO's is comparable. Some of the perpendicular sum rules seem to be slightly better in the GTO basis, indicating that our π-basis set is probably less complete than that of Martin *et al.*[36] This finding might be rather surprising since it is normally argued that comparable results are obtained with a GTO/STO-ratio of not less than 3.[37] This conclusion is, however, based on consideration of properties connected with the ground state and other low lying states. Since continuum one-electron states look neither like STO's nor like GTO's, there is no reason to believe the STO's should give a better discrete representation of the continuum. Furthermore the rather substantial deviations between the dipole length and the dipole velocity results for $S(2)$ and $S(1)$ demonstrate that we have a far from complete description of the continuum.

The excitation spectrum in Table I shows the same trends as observed earlier,[17,28] namely that (i) excitation energies are consistently higher in SPPA than in

TABLE VIII. Indirect nuclear spin–spin coupling constant (in cps) evaluated for HD at $R = 1.40$ bohr.

Method	Results
Hartree–Fock	29.74
Mono-excited CI	40.09
TDHF	59.97
SPPA	46.42
SPPA with $2p$–$2h$ corrections	46.95
Kowalewski *et al.*[a]	43.26
Experiment[b]	42.94

[a]Results from Ref. 13 without vibrational averaging. See also Table 4 of this reference for a comprehensive review of earlier calculations.

[b]H. Benoit and P. Piejus, C. R. Acad. Sci. (Paris) B265, 101 (1967).

TABLE IX. The lowest vertical excitation energies, ω_{on} (in eV), and corresponding oscillator strengths in the dipole length, f_L, and the dipole velocity formulation, f_V, calculated for hydrogen fluoride at $R = 1.733$ bohr using the basis set of Ref. 39. All excitations are from the $^1\Sigma^+$ ground state.

Final state		$^1\Sigma^+$	$^1\Sigma^+$	$^1\Sigma^-$	$^1\Pi$	$^1\Pi$	$^1\Delta$	$^1\Delta$	$^3\Sigma^+$	$^3\Sigma^+$	$^3\Sigma^-$	$^3\Pi$	$^3\Pi$	$^3\Delta$
	ω_{on}	15.92	18.27	15.60	12.72	19.07	15.59	20.12	14.11	15.60	14.87	11.82	18.85	15.27
MECI	f_L	0.035	0.386		0.023	0.016								
	f_V	0.038	0.249		0.024	0.011								
	ω_{on}	15.88	18.01	15.57	12.65	19.04	15.57	20.12	13.62	15.57	14.74	11.68	18.79	15.20
TDHF	f_L	0.030	0.342		0.024	0.016								
	f_V	0.038	0.349		0.017	0.013								
	ω_{on}	17.18	19.54	16.71	14.19	20.59	16.69	21.11	15.73	16.70	16.22	13.28	20.37	16.37
SPPA	f_L	0.007	0.399		0.028	0.017								
	f_V	0.009	0.336		0.021	0.011								
	ω_{on}	14.15	17.02	13.83	11.63	18.24	13.77	18.23	13.24	14.51	13.59	10.94	18.10	13.59
$2p-2h$	f_L	0.001	0.358		0.024	0.016								
	f_V	0.001	0.412		0.027	0.013								
CI[a]	ω_{on}	13.99	16.62	13.65	10.98	17.40	13.27	17.80	13.13	13.63	13.64	10.40	17.30	13.23
	f_L	0.01	0.39		0.03	0.02								

[a]Results of the CI calculation of Bender and Davidson, Ref. 39.

TDHF; (ii) the effect is more pronounced in triplet than in singlet; (iii) the $2p-2h$ corrections will lower the SPPA-excitation energies, especially in singlet; and (iv) the net effect is a substantial improvement of the triplet TDHF-spectrum and an almost equally good singlet spectrum in TDHF and SPPA corrected with $2p-2h$ excitations. The calculated excitation frequencies are, however, all slightly too high, particularly for singlets. Presently,[28] the calculation of $2p-2h$ correction is based on consideration of the diagonal elements of $\mathbf{A}_{II}$ alone [Eq. (29)] and those elements are furthermore approximated with orbital energy differences. Although this procedure gives the major changes in the excitation spectra, a more accurate treatment of $\mathbf{A}_{II}$ elements is needed and investigation of this problem is under way.

For the oscillator strengths in Table I, the tendency is also clear: Improved agreement between the dipole length and the dipole velocity results when going from MECI to TDHF and from SPPA to $2p-2h$. The two formulations are, as stated before, exactly equivalent in TDHF[21] but not necessarily in SPPA and in SPPA with $2p-2h$ corrections. Due to our choice of basis functions the agreement is best in TDHF even though the $2p-2h$ results are nearly equivalent. The changes in oscillator strength caused by inclusion of $2p-2h$ excitations originate from both transition moments and excitation energies. In most cases the energy change is responsible for the major effect, but Table I shows that for the $X\,^1\Sigma_g^+$ to $B\,^1\Sigma_u^+$ excitation, for example, the trends in excitation energy and the dipole length oscillator strength are opposite. To illustrate this point further we have in Table V listed the transition moments for the two lowest allowed σ transitions. This table shows that the changes in transition moments in most cases are more pronounced when going from SPPA to SPPA with $2p-2h$ corrections than going from TDHF to SPPA. Even though those changes are always smaller than the difference between the TDHF and MECI moments, it seems, for certain excitations, to be important to estimate the effect of $2p-2h$ excitations on the transition moments. This conclusion disagrees slightly with the one reached by Shibuya *et al.*[27]

Dalgarno and Epstein[19] have shown that it is possible to have certain sum rules for oscillator strengths fulfilled exactly if the basis set contains the product of the perturbing operator (e.g., $\mathbf{r}$) and the ground state wavefunction. Calculations where basis functions are chosen according to this criterion give very accurate results for polarizabilities and Van der Waals forces.[8,9] The sum rules in Table III show that our basis set does not fulfill the Dalgarno–Epstein requirement. Consequently the polarizabilities and dispersion forces in Tables VI and VII are not as accurate as those obtained by either much larger[38] or more carefully chosen[9] basis sets. It is, however, clear that improvement in polarizabilities

TABLE X. The lowest TDHF-transition energies, ω_{on} (in eV), and corresponding oscillator strengths for hydrogen fluoride. Designations and constants are the same as in Table IX except that we have used the basis set of Cade and Huo.[a]

Final state	ω_{on}	f_L	f_V
$^1\Sigma^+$	18.44	0.395	0.398
$^1\Sigma^+$	27.70	0.088	0.086
$^1\Sigma^-$	24.04		
$^1\Pi$	13.75	0.020	0.013
$^1\Pi$	25.80	0.060	0.035
$^1\Delta$	24.35		
$^1\Delta$	38.24		
$^3\Sigma^+$	14.15		
$^3\Sigma^+$	24.04		
$^3\Sigma^-$	20.85		
$^3\Pi$	12.55		
$^3\Pi$	24.53		
$^3\Delta$	22.83		

[a]Reference 40.

TABLE XI. Static dipole polarizabilities for hydrogen fluoride at $R = 1.733$ bohr. Calculated with the basis set given in Ref. 39. Atomic units.

	$\alpha_{\parallel}$		$\alpha_{\perp}$		α	
	Length	Velocity	Length	Velocity	Length	Velocity
Hartree–Fock	6.25	4.17	2.51	1.86	3.75	2.62
Mono-excited CI	6.01	3.78	2.52	1.92	3.68	2.54
TDHF	5.24	4.98	2.40	2.00	3.39	3.00
SPPA	4.93	4.00	2.29	1.72	3.17	2.48
SPPA + $2p$–$2h$	5.38	5.51	2.50	2.27	3.46	3.35
KK[a]	5.34		2.46		3.42	
SL[b]	5.80		4.20		4.73	
Epstein[c]	5.33	6.15	4.04	4.36	4.47	4.95

[a]M. Karplus and H. J. Kolker, J. Chem. Phys. 39, 2011 (1963).
[b]R. M. Stevens and W. N. Lipscomb, J. Chem. Phys. 41, 184 (1964).
[c]I. R. Epstein, Ref. 45.

and related quantities closely follow improvements in the sum rules, i.e., the best results are obtained in TDHF and an increase in the size of the basis set will further improve the sum rules.

It is in this communication, however, not our aim to try to reproduce very accurate results but instead to show how TDHF-like schemes can be used to evaluate several different properties in the same calculation. Therefore, we have with the same basis set also computed the indirect nuclear spin–spin coupling constant for HD. The results are given in Table VIII. This table demonstrates that the SPPA results, with or without the $2p$–$2h$ corrections, are much better than the TDHF values. As stated before, the spin–spin coupling constant is a "triplet" property which means that it is rather poorly determined in TDHF as compared with SPPA, the same tendency as was seen in the excitation spectrum in Table I. The good agreement between MECI and the experimental value is of course purely accidental. Since the basis set is fixed, the results in Table VIII show the importance of electronic correlation when going from HF with no correlation to SPPA where both the ground state and excited states are correlated. We believe that the remaining disagreement between our results and that of Kowalewski *et al.*[13] is due mainly to the incompleteness of our basis set.

V. RESULTS FOR HYDROGEN FLUORIDE

The excitation spectrum for HF was computed using the basis sets of Bender and Davidson[39] (33 STO's) and of Cade and Huo[40] (32 STO's). The results for the lowest transitions are given in Table IX and Table X. The basis set of Cade and Huo was determined from a minimization of the ground state energy in the Hartree–Fock approximation. For a description of excited states it is, as seen for H_2, necessary to introduce less contracted STO's in the basis set. For hydrogen fluoride this was done by Bender and Davidson.[39] Their basis set, consisting of 33 STO's is of the same size as that of Cade and Huo. The exponents were chosen to reproduce, as accurately as possible, the charge density of the ground state as given by Cade and Huo[40] at the experimental internuclear separation, $R = 1.733$ bohr. Tables IX and X show that only for the very lowest excitations do the two basis sets give comparable results. As for H_2 we have also calculated energy weighted sum rules. The results of those, together with the very large excitation energies in Table X, make it clear that the basis set of Bender and Davidson[39] gives a superior description of properties connected with excited states.

Since all numbers in Table IX are produced with the same basis set a direct comparison is possible. The trends in our results are the same as those already commented on for H_2, except that here the effect of the $2p$–$2h$ excitations is slightly more pronounced. This is probably due to the fact that we in HF have more than two valence electrons. This means that the $2p$–$2h$ corrections will introduce correlations among electrons in occupied MO's, an effect which is not present in H_2.[28] The excitation frequencies and corresponding oscillator strengths agree quite well with those found by Bender and Davidson,[39] even though our final excitation energies seem to be slightly larger, especially in the singlet case. The deviations stem from the different choice of configurations in SPPA with $2p$–$2h$ corrections and in the selective CI method of Bender and Davidson.[39,41]

Very little is known experimentally about the absorption spectrum of HF. Waggoner *et al.*[42] have reported a very sharp absorption peak at 13.0 eV, which they assigned to the lowest $X\,^1\Sigma^+ \rightarrow {}^1\Pi$ transition ($N \rightarrow Q$ transition). Di Lonardo and Douglas[43] have observed the same transition at 13.03 eV and an $X\,^1\Sigma^+ \rightarrow a\,^3\Pi$ transition at slightly lower energy. (They do not say how much lower.) All these observations seem to agree with our calculated spectrum. Our value of 11.63 eV for the $N \rightarrow Q$ transition is closer to the experimental value than that

TABLE XII. Dispersion-force coefficients[a] for a pair of hydrogen fluoride molecules with $R = 1.733$ bohr. Atomic units.

	C		Γ		Δ	
	Length	Velocity	Length	Velocity	Length	Velocity
Hartree–Fock	10.2	4.85	0.33	0.29	0.11	0.08
TDHF	8.03	6.30	0.28	0.32	0.08	0.10
SPPA + $2p$–$2h$	8.23	7.32	0.27	0.32	0.08	0.10

[a]For a definition of C, Γ, and Δ, see Ref. 30.

TABLE XIII. Indirect nuclear spin–spin coupling constant (in cps) for hydrogen fluoride at $R = 1.733$ bohr.

Hartree–Fock	307.9[a]		294.1[b]
Mono excited CI	506.4[a]		610.6[b]
TDHF	783.5[a]		1018.6[b]
SPPA	669.2[a]		829.1[b]
SPPA with $2p$–$2h$ corrections	643.7[a]		760.8[b]
CNDO[c]		−150.3	
INDO[c]		19.7	
Kato and Saika[d]		528.1	
Murrell *et al.*[e]		835.6	
Experiment[f]	577[g]		589 ± 23[h]

[a]Evaluated with the basis set of Bender and Davidson, Ref. 39.
[b]Evaluated with the basis set of Cade and Huo, Ref. 40.
[c]Semiempirical values taken from J. A. Pople and D. L. Beveridge, *Approximate Molecular Orbital Theory* (McGraw–Hill, New York, 1970) p. 157.
[d]From Ref. 47 taken into account the numerical error detected by Murrell *et al.* in Ref. 49.
[e]SCF + CI results from Ref. 49.
[f]In both experimental values the orbital and spin-dipolar terms are subtracted, estimated from Kato and Saika[47] to be −60 cps.
[g]C. MacLean and E. L. Mackor, Proc. XI Colloq. AMPERE 1962, 571.
[h]J. S. Muenter and W. Klemperer, J. Chem. Phys. **52**, 6033 (1970).

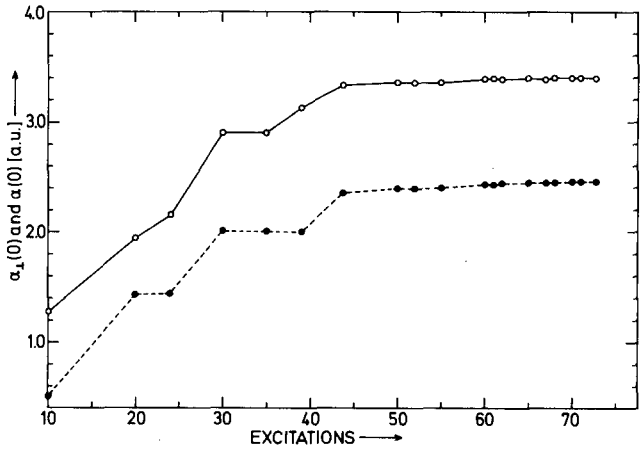

FIG. 2. The frequency independent polarizabilities $\alpha_\perp(0)$ [---] and $\alpha(0)$ [——] for hydrogen fluoride [defined in Eqs. (35)–(37) of the text] versus the number of excitations included in the sum over excited states. The excitations are arranged in order of increasing energies. SPPA + $2p$–$2h$ results are used.

found by Bender and Davidson.[39] The singlet–triplet excitation reported in Ref. 43 is here predicted to lie at 10.94 eV. Like Bender and Davidson, we do find a very strong transition around 17 eV, which can be assigned to the "charge transfer" state ($N \rightarrow V$ transition). A transition of this type was observed by Waggoner *et al.*[42] but was not nearly as strong as predicted by the two calculations.

We have in Fig. 1 plotted the frequency-dependent dynamic dipole polarizability as calculated in SPPA with $2p$–$2h$ corrections. Results in different approximations for the frequency independent polarizabilities and dispersion-force coefficients are listed in Tables XI and XII, respectively. Comparison is made with the time dependent coupled Hartree–Fock[44] calculations of Epstein.[45] He used a smaller basis set than we do (19 STO's for $\alpha_\parallel$) but the exponents were varied to give an optimal description of second order properties. The basis set of Bender and Davidson[39] is not optimized in the same fashion and we do find that the sum rules for oscillator strengths show deviation from the correct results, especially for the perpendicular components. Following our experience from H_2 this might indicate that also the polarizabilities will be less accurate. We can from Table XI and Fig. 1 see that our results in fact do disagree with those of Epstein[45] even if we assume that the error bars on ours are given by the difference between the dipole length and dipole velocity results. Other calculations, some of which are included

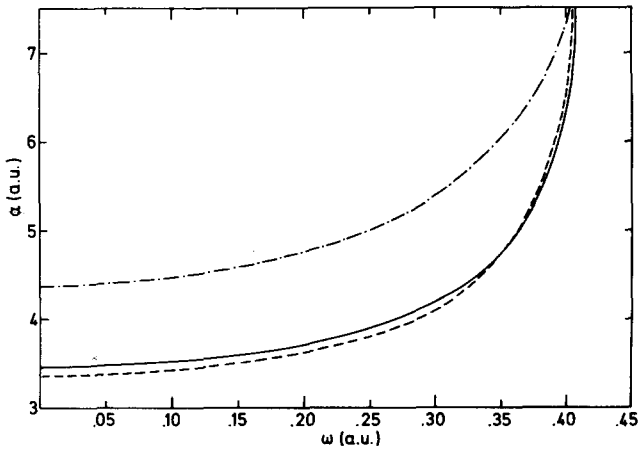

FIG. 1. The frequency dependent dynamic dipole polarizability, $\alpha(\omega)$, for HF. Our results are given in SPPA corrected with two-particle, two-hole excitations in the dipole length (–) and the dipole velocity (----) formulation, respectively. For comparison, the polarizability from Ref. 45 is also plotted (–·–·–).

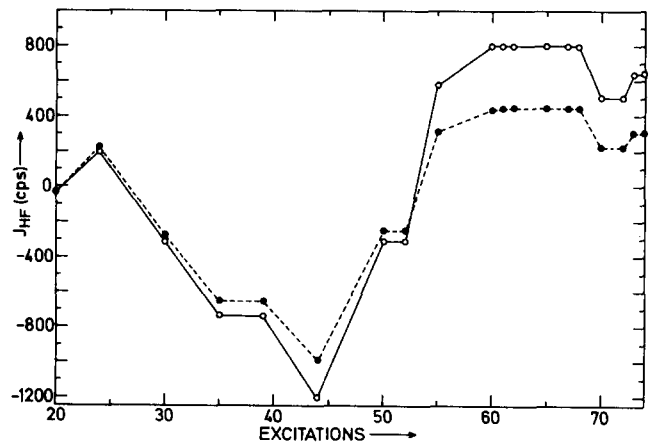

FIG. 3. The indirect nuclear spin–spin coupling constant for HF, J_{HF}, plotted as functions of the number of particle–hole excitations included in the sum in Eq. (46) of the text. The dotted line indicates Hartree–Fock results and the solid lines are SPPA results corrected with $2p$–$2h$ excitations. The excitations are arranged in order of increasing energies.

in Table XI, give polarizabilities which are closer to ours, but lack of experimental results makes it impossible to make definite statements about the reliability of the different calculations.

We have in Fig. 2 investigated the error introduced by the truncation in the sum over excited states in Eqs. (35) and (36). $\alpha_\perp(0)$ and $\alpha(0)$ are plotted as functions of the number of excitations included in those sums. Both curves show a clear convergence. Notice, though that it is necessary to go beyond 50 excitations before the levelling off occurs. The results are given in SPPA with $2p$–$2h$ corrections but the convergence is the same in Hartree–Fock or any of the other approximations examined.

In the basis that was used to calculate static polarizabilities, Epstein[45] also computed the lowest $^1\Sigma^+ \rightarrow {}^1\Pi$ and $^1\Sigma^+ \rightarrow {}^1\Sigma^+$ transition frequencies to be 12.21 and 15.85 eV, respectively. Both values are larger than those given in the last two rows in Table IX, and especially the $^1\Sigma^+ \rightarrow {}^1\Sigma^+$ lies substantially higher. Epstein[45] also quotes excitation energies for H_2 which are about 1 eV too high. In calculations[46] on He_2, we have observed that excitation energies usually are too high when calculated from "smaller" basis sets which are optimized to fulfill certain oscillator sum rules. It seems as if this trend also holds for HF (and H_2).

The first extensive calculation of the indirect nuclear spin-spin coupling constant for HF was performed by Kato and Saika.[47] They applied a sum-over-states perturbation procedure. Hartree–Fock excited states were used, i.e., in the ground state wavefunction, one occupied MO was replaced with a virtual HF orbital. A similar procedure was followed by Adam *et al.*[48] In neither of the two calculations did they observe any convergence in the sum-over-states expansion. Murrell *et al.*[49] found that introduction of configuration interaction in a small basis did not solve the convergence problem either. We have examined this problem and our results in Hartree–Fock and SPPA corrected with two-particle, two-hole excitations are given in Fig. 3. The spin–spin coupling constant is plotted as a function of the number of particle–hole excitations (l, k) included in the sum in Eq. (46). This is exactly equivalent to inclusion of variable number of states in sum-over-states procedures. The oscillations in J_{HF} are strongest when less than 55 excitations are included in the summation. Between 55 and 75 excitations a noticeable "damping" of those oscillations occurs, which probably indicates that we are approaching convergence of the sum in Eq. (46). Results with more than 75 excitations are needed for a definite conclusion about the convergence but the present computer facilities do unfortunately not allow us to go beyond 75 excitations. Earlier published results[47–49] do not include more than 45 excitations[48] which (with reference to Fig. 3) might explain why no one so far has been able to reach convergence in the sum-over-states procedures. The data in Fig. 3 also show that the convergence is not affected by introduction of correlation. The convergence is the same in Hartree–Fock as in SPPA with $2p$–$2h$ corrections. Correlation does, however, significantly improve the numerical value of the calculated spin–spin coupling constant. The same conclusions were reached by Murrell *et al.*[49] for a calculation using a much smaller basis set.

In Table XIII we have collected all our final results together with those of other investigations. We have used the Cade–Huo[40] and Bender–Davidson[39] basis sets. Both give spin–spin coupling constants of the same magnitude, even though the latter, as expected, gives the best agreement with the experiments. The fact that the two rather different basis sets produce results of comparable magnitude seems to support our previous statement concerning the convergence of the sum-over-states expansion. Our final results (SPPA + $2p$–$2h$ corrections) are both larger than the estimated experimental values. This might be due to an underestimate of the orbital and spin–dipolar terms in the quoted experimental values.

VI. CONCLUSION

We have in the preceding sections demonstrated how a self-consistent TDHF procedure advantageously can be used in *ab initio* calculations of second order properties. We have here applied the method to diatomic molecules, but in principle SPPA calculations can be performed for any system for which it is feasible to generate a Hartree–Fock, multiconfiguration self-consistent field[50] or similar molecular orbital basis. The only quantities needed are the integrals in the MO basis.

The self-consistent procedure is rapidly convergent. Typically, three to four iterations suffice. The actual computing time for an *ab initio* SPPA calculation varies from 10 to 100 per cent of that of the preceding HF calculation. Almost all the time is spent on integral retrieval. If it was possible to keep the integrals in fast core this time could be reduced considerably. This implies that in semiempirical applications the computing time for SPPA is negligible.[17] At any rate, considering the much larger computation effort involved in comparable CI calculations, SPPA is an economical way of generating nearly the same information. Furthermore SPPA gives at no extra cost transition moments and related quantities such as polarizabilities which are seldom available from CI calculations because of the difficulty of evaluating them from large wavefunctions if different orbitals for different states are used.

ACKNOWLEDGMENTS

We would like to thank Jan Linderberg for encouragement and support, and the Regional Data Center of Aarhus University for grants of computer time.

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