Ab initio calculations on bent-chain models of solid hydrogen fluoride

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Ab initio Hartree-Fock and Møller-Plesset perturbation-theoretical correlation calculations have been performed on a bent hydrogen fluoride chain, modeling solid hydrogen fluoride. It has been found that the lowering of the ionization potential with respect to the monomer is a pure correlation effect, due in considerable part to third-order contributions in the case of the monomer. Finally, the influence of the second-order irreducible vertex part on the exciton binding energies is discussed.

I. INTRODUCTION

Hydrogen fluoride in the solid phase forms long bent hydrogen-bonded chains with large interchain distances.[1] Therefore, one-dimensional zigzag chains can be considered as models for solid hydrogen fluoride. This and a general interest in simple models of hydrogen-bonded systems has triggered several calculations on (finite and infinite) chains of hydrogen fluoride molecules.[2–9] Although most of the calculations have been performed at the *ab initio* level, electron correlation has been included in only one of them[9] for tetrameric clusters, never, however, for the infinite chain. The present study is concerned with the influence of correlation on important electronic properties of the infinite hydrogen fluoride chain as band structures and exciton binding energies.

The calculated quantities will be related to corresponding observables of the free HF molecule. Nevertheless these relations are by no means trivial, and in some cases even have been the subject of controversies. For instance, the ionization potential of the infinite HF chain is by some calculations predicted to be lower,[3,5] by other calculations to be higher,[7] than the ionization potential of the free HF molecule. Accurate calculations including electron correlation are desirable here, the more so because experimental results for the ionization potential of the HF crystal seem not yet to be available.

Finally, there is another more theoretical motivation for studying the infinite HF chain, namely that it represents one of the simplest, but still realistic, model systems for polymer calculations. In fact, some higher-order correlation corrections, as, e.g., the third-order corrections to the quasiparticle bands[10] or the second-order irreducible vertex parts in exciton calculations,[11] could until now be applied only to model systems consisting of hydrogen atoms and the treatment of the HF chain with these methods constitutes then a test for their capability to treat more complex systems.

II. MØLLER-PLESSET PERTURBATION THEORY FOR THE QUASIPARTICLE BANDS

To calculate electron correlation effects in an infinite system requires a size-consistent method.[12] We have used the Møller-Plesset scheme,[13] which means to chose as unperturbed problem the Hartree-Fock equations. These equations, formulated for an infinite chain in the linear combination of atomic orbital (LCAO) approximation, are known as the crystal orbital equations[14] and will be solved for the HF chain with three different basis sets (minimal,[15] double zeta,[9] and double zeta with a p function at the hydrogen) using the experimental geometry[1] (1.02 Å for the H—F bond length, 2.49 Å for the F-F distance, and 120.1° for the F—F—F angle). Up to three $(HF)_2$ elementary cells were included in the Hartree-Fock calculations, and the first neighboring $(HF)_2$ cells were included in the calculation of the quasiparticle band shifts.

The four-index transformation from the atomic-orbital to the crystal-orbital basis is performed stepwise:[13] first to determine localized Wannier functions, then to transform the two-electron integrals from the atomic orbital to the Wannier-function basis, and finally to transform them from the Wannier-function to the crystal-orbital basis.

The quasiparticle bands are then calculated as solutions of the inverse Dyson equation[16] in diagonal approximation:

$$\omega_{\mathscr{I}}=\epsilon_{\mathscr{I}}+M_{\mathscr{I}\mathscr{I}}(\omega_{\mathscr{I}}) , \tag{1}$$

where $\mathscr{I}$ is a composite index, comprising the band index and k index, i.e., $\mathscr{I}=(i,k_i)$; $\epsilon_{\mathscr{I}}$ describes the crystal-orbital band structure, $\omega_{\mathscr{I}}$ the quasiparticle band structure and $M_{\mathscr{I}\mathscr{I}}$ is the irreducible self-energy part (the spin indices can be eliminated for a closed-shell system).

The expansion of M up to third order is[10]

$$M_{PQ}=M_{PQ}^{(2)}+M_{PQ}^{(3A)}+M_{PQ}^{(3C)}+M_{PQ}^{(3D)} .$$

with

$$M_{PQ}^{(2)}(\omega)=\sum_{JKL}V_{PJKL}(2V_{KLQJ}-V_{KLJQ})\delta_{k_p,k_q}\delta_{k_j,k_k+k_l-k_p}$$
$$\times[n_J\bar{n}_K\bar{n}_L(\omega+\epsilon_J-\epsilon_K-\epsilon_L+i\eta)^{-1}+\bar{n}_Jn_Kn_L(\omega+\epsilon_J-\epsilon_K-\epsilon_L-i\eta)^{-1}] ,$$

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$$
\begin{aligned}
M_{PQ}^{(3A)} = \sum_{J,K,L,M,N} & (2V_{PNQM} - V_{PNMQ})(2V_{MJKL} - V_{MJLK}) V_{KLNJ} \delta_{k_p,k_q} \delta_{k_n,k_m} \delta_{k_j,\, k_k + k_l - k_m} \\
& \times [-n_J \bar{n}_K \bar{n}_L n_M n_N (\epsilon_M + \epsilon_J - \epsilon_K - \epsilon_L + i\eta)^{-1} (\epsilon_N + \epsilon_J - \epsilon_K - \epsilon_L + i\eta)^{-1} \\
& \quad + \bar{n}_J n_K n_L \bar{n}_M \bar{n}_N (\epsilon_K + \epsilon_L - \epsilon_J - \epsilon_M + i\eta)^{-1} (\epsilon_K + \epsilon_L - \epsilon_J - \epsilon_N + i\eta)^{-1} \\
& \quad + n_J \bar{n}_K \bar{n}_L n_M \bar{n}_N (\epsilon_M + \epsilon_J - \epsilon_K - \epsilon_L + i\eta)^{-1} (\epsilon_M - \epsilon_N + i\eta)^{-1} \\
& \quad + n_J \bar{n}_K \bar{n}_L \bar{n}_M n_N (\epsilon_N + \epsilon_J - \epsilon_K - \epsilon_L + i\eta)^{-1} (\epsilon_N - \epsilon_M + i\eta)^{-1} \\
& \quad - \bar{n}_J n_K n_L n_M \bar{n}_N (\epsilon_K + \epsilon_L - \epsilon_J - \epsilon_N + i\eta)^{-1} (\epsilon_M - \epsilon_N + i\eta)^{-1} \\
& \quad - \bar{n}_J n_K n_L \bar{n}_M n_N (\epsilon_K + \epsilon_L - \epsilon_J - \epsilon_M + i\eta)^{-1} (\epsilon_N - \epsilon_M + i\eta)^{-1}] ,
\end{aligned}
\tag{2}
$$

$$
\begin{aligned}
M_{PQ}^{(3C)}(\omega) = \sum_{J,K,L,M,N} & (2V_{PJMN} - V_{PJNM}) V_{MNKL} V_{KLQJ} \delta_{k_p,k_q} \delta_{k_j,\, k_m + k_n - k_p} \delta_{k_l,\, k_m + k_n - k_k} \\
& \times [n_J \bar{n}_K \bar{n}_L \bar{n}_M \bar{n}_N (\omega + \epsilon_J - \epsilon_K - \epsilon_L + i\eta)^{-1} (\omega + \epsilon_J - \epsilon_M - \epsilon_N + i\eta)^{-1} \\
& \quad + n_J n_K n_L \bar{n}_M \bar{n}_N (\epsilon_K + \epsilon_L - \epsilon_M - \epsilon_N + i\eta)^{-1} (\omega + \epsilon_J - \epsilon_M - \epsilon_N + i\eta)^{-1} \\
& \quad + n_J \bar{n}_K \bar{n}_L n_M n_N (\omega + \epsilon_J - \epsilon_K - \epsilon_L + i\eta)^{-1} (\epsilon_M + \epsilon_N - \epsilon_K - \epsilon_L + i\eta)^{-1} \\
& \quad + \bar{n}_J \bar{n}_K \bar{n}_L n_M n_N (\omega + \epsilon_J - \epsilon_M - \epsilon_N - i\eta)^{-1} (\epsilon_M + \epsilon_N - \epsilon_K - \epsilon_L + i\eta)^{-1} \\
& \quad + \bar{n}_J n_K n_L \bar{n}_M \bar{n}_N (\epsilon_K + \epsilon_L - \epsilon_M - \epsilon_N + i\eta)^{-1} (\omega + \epsilon_J - \epsilon_K - \epsilon_L - i\eta)^{-1} \\
& \quad - \bar{n}_J n_K n_L n_M n_N (\omega + \epsilon_J - \epsilon_K - \epsilon_L - i\eta)^{-1} (\omega + \epsilon_J - \epsilon_M - \epsilon_N - i\eta)^{-1}] ,
\end{aligned}
$$

$$
\begin{aligned}
M_{PQ}^{(3D)}(\omega) = \sum_{J,K,L,M,N} & \{ V_{PNMJ} [V_{MLNK} (V_{KJQL} - 2V_{JKQL}) + V_{MLKN} (V_{JKQL} - 2V_{KJQL})] \\
& \quad + V_{PNJM} [V_{MLNK} (4V_{JKQL} - 2V_{KJQL}) + V_{MLKN} (V_{KJQL} - 2V_{JKQL})] \} \\
& \times \delta_{k_p,k_q} \delta_{k_l,\, k_k + k_n - k_m} \delta_{k_j,\, k_p + k_n - k_m} \\
& \times [\bar{n}_J \bar{n}_K n_L \bar{n}_M n_N (\omega + \epsilon_N - \epsilon_M - \epsilon_J + i\eta)^{-1} (\omega + \epsilon_L - \epsilon_J - \epsilon_K + i\eta)^{-1} \\
& \quad + \bar{n}_J n_K \bar{n}_L \bar{n}_M n_N (\omega + \epsilon_N - \epsilon_M - \epsilon_J + i\eta)^{-1} (\epsilon_K + \epsilon_N - \epsilon_L - \epsilon_M + i\eta)^{-1} \\
& \quad + \bar{n}_J \bar{n}_K n_L n_M \bar{n}_N (\epsilon_L + \epsilon_M - \epsilon_K - \epsilon_N + i\eta)^{-1} (\omega + \epsilon_L - \epsilon_J - \epsilon_K + i\eta)^{-1} \\
& \quad + n_J \bar{n}_K n_L n_M \bar{n}_N (\epsilon_L + \epsilon_M - \epsilon_K - \epsilon_N + i\eta)^{-1} (\omega + \epsilon_N - \epsilon_J - \epsilon_M + i\eta)^{-1} \\
& \quad + n_J n_K \bar{n}_L \bar{n}_M n_N (\omega + \epsilon_L - \epsilon_J - \epsilon_K - i\eta)^{-1} (\epsilon_K + \epsilon_N - \epsilon_L - \epsilon_M + i\eta)^{-1} \\
& \quad - n_J n_K \bar{n}_L n_M \bar{n}_N (\omega + \epsilon_L - \epsilon_J - \epsilon_K - i\eta)^{-1} (\omega + \epsilon_N - \epsilon_M - \epsilon_J - i\eta)^{-1}] ,
\end{aligned}
$$

where $V_{\mathscr{I}JKL} = \langle \mathscr{I}(1)J(2) \mid K(1)L(2) \rangle$ are the two-particle integrals over crystal orbitals, $n_{\mathscr{I}}$ the occupation numbers ($n_{\mathscr{I}} = 1$ for a doubly occupied $n_{\mathscr{I}} = 0$ for an empty band), $\bar{n}_{\mathscr{I}} = 1 - n_{\mathscr{I}}$, and η is a positive infinitesimal, tending to zero in the distributional sense.

The results for the upper valence band edge and the lower conduction-band edge are given in Table I. We have in all cases omitted the core bands in the summations and as a further approximation for the third order we have evaluated $M^{(3)}$ at fixed position $\epsilon_{\mathscr{I}}$ and took only six bands into account for the virtual excitations occurring in $M^{(3)}$. Besides the energies also the renormaliza-

tion factors

$$P_{\mathcal{F}} = \left[1 - \frac{\partial M_{\mathcal{F}\mathcal{F}}}{\partial \omega} \bigg|_{\omega_{\mathcal{F}}} \right]^{-1}$$

evaluated in second order are given in parentheses.

The correlation effects shift the valence band up and the conduction band down, thus decreasing the band gap. The third-order contributions go into the same direction as the second-order corrections, but are much smaller in magnitude. In the case of the second-order results for minimal and double-zeta basis sets we have, in addition, listed the band widths, which also show appreciable changes upon inclusion of correlation.

It is interesting to compare the trends for the ionization potential with the corresponding trends for the HF monomer. We have performed calculations at the corresponding levels of approximation (experimental geometry from Ref. 17) and listed the results also in Table I. [For other Green's-function calculations on the ionization potential (IP) of the HF monomer see, e.g., Refs. 18 and 19.]

As mentioned in the Introduction, Bassani *et al.*[3] and Zunger[5] obtain using Koopman's approximation a lower IP for the HF chain than for the HF monomer. This corresponds to our minimal and double-zeta results for $-\epsilon_I$. Karpfen,[7] on the other hand, obtains a slightly higher IP for the chain, as is reproduced by our double-zeta plus p-function calculation.

After taking correlation into account the IP is given by $-\omega_{\mathcal{F}}$ where $\omega_{\mathcal{F}}$ is the corresponding pole of the one-particle Green's function as listed in the table. In this case the IP of the chain is lower than the IP of the monomer by about 1 eV for all basis sets. In view of the different results in Koopman's approximation this lowering must be seen as a pure correlation effect. A considerable part of the shift comes from the behavior of the third-order contributions in the case of the monomer, which is opposite for the chain than for the monomer.

Although the convergence of the perturbation expansion for the IP's is generally not so fast as for the ground-state correlation energy (where in the case of the HF monomer already the second order covers about 97% of the fourth-order correlation energy[20]), it still seems possible to estimate the remaining error due to a finite-order expansion and, first of all, due to basis set effects to be of the order of 0.2–0.3 eV. (The total Hartree-Fock monomer ground-state energies for our basis sets were −99.3756 a.u., −100.0011 a.u., and −100.0265 a.u. while the Hartree-Fock limit[21] is −100.0705 a.u.) This is supported by comparison of the Koopman's IP of the monomer (17.54 eV) with the Hartree-Fock limit value of 17.70 eV (Ref. 20) as well as by estimates for similar correlation calculations on the monomer IP.[18,22,23] [One should point out that though by correlation calculations the total energy becomes larger in absolute value (more negative), the IP with correlation becomes smaller in absolute value, in our case 16.01 eV for the monomer and 15.09 eV for the polymer; see Table I.] An experimental value for the IP of HF crystal is not available to our knowledge, but from the agreement of the calculated monomer IP with the experimental value of 16.19 eV (Ref. 19) we can expect for the crystal an IP of about 15 eV.

TABLE I. Quasiparticle band-structure data for the bent HF chain in comparison to the HF molecule. (All energies in eV.)

		HF		$(HF)_x$		
		V[a]	C[b]	V[c]	C[d]	E_{gap}
MB[e]	$\epsilon_{\mathcal{F}}$	−16.04	14.80	−15.48	11.43	26.91
	$\Delta\epsilon_{(2)}$[f]			0.33	3.26	
	$\omega_{\mathcal{F}}$	−14.91	15.16	−13.90	11.34	25.24
	$P_{\mathcal{F}}^{(2)}$	(0.971)	(0.972)	(0.952)	(0.979)	
	$\Delta\omega_{(3)}$[g]			1.23	3.22	
	$\omega_{\mathcal{F}}$	−14.99	15.27	−13.85	11.30	25.15
DZ[h]	$\epsilon_{\mathcal{F}}$	−17.63	3.39	−17.35	3.46	20.81
	$\Delta\epsilon_{(2)}$[f]			0.25	2.86	
	$\omega_{\mathcal{F}}$	−15.33	3.34	−15.07	3.22	18.29
	$P_{\mathcal{F}}^{(2)}$	(0.946)	(0.996)	(0.933)	(0.988)	
	$\Delta\omega_{(3)}$[g]			1.45	2.97	
	$\omega_{\mathcal{F}}$	−16.17	3.40	−15.06	3.21	18.27
DZP[i]	$\epsilon_{\mathcal{F}}$	−17.54	3.50	−17.57	3.57	21.14
	$\omega_{\mathcal{F}}^{(2)}$	−15.29	3.42	−15.10	3.05	18.15
	$P_{\mathcal{F}}^{(2)}$	(0.947)	(0.996)	(0.918)	(0.986)	
	$\omega_{\mathcal{F}}^{(3)}$	−16.01	3.49	−15.09	3.03	18.12

[a]Highest occupied orbital.
[b]Lowest unoccupied orbital.
[c]Upper valence-band edge.
[d]Lower conduction-band edge.
[e]Minimal basis (MB) set results.
[f]Band widths in the Hartree-Fock approximation.
[g]Band widths in the second-order approximation.
[h]Double-zeta (DZ) basis set results.
[i]Double-zeta plus p-function (DZP) basis set results.

III. EXCITON BINDING ENERGY

Excitons constitute *per se* a correlation effect because the Coulomb and exchange integrals, which would be responsible for the electron-hole binding in a single-determinant picture, tend to zero in the infinite-size limit,[24] and only electron correlation leads to a nonzero binding energy.

The corresponding framework for *ab initio* calculations is the so-called intermediate exciton theory.[25–29] Several calculations on infinite chains have been performed within this framework,[11,28,29] most of them, however, only with first-order irreducible vertex parts.

The inclusion of second-order corrections to the irreducible vertex parts has only recently been discussed, and applications have so far been reported only for alternating hydrogen chains.[11] Application of the formalism to the HF chain may, therefore, provide a useful further test case. The exciton energies were calculated (for given K) from the following secular equation:

$$\det[\underline{\mathbb{1}}-\underline{\mathscr{G}}^{(0)}(K,\omega)\underline{\mathscr{K}}(K,\omega)]=0\ , \tag{3}$$

where $\underline{\mathscr{G}}^{(0)}$ and $\underline{\mathscr{K}}$ are the matrices of the interaction-free particle-hole Green's function and the irreducible vertex part, respectively, both in exciton representation, i.e.,

$$\mathscr{G}^{(0)}_{H'H}(K,\omega)=N^{-1}\sum_{k_i,k_j}\exp[ik_i(H'-H)]\delta_{k_i-k_j,K}P_IP_J/(\omega-\omega_I+\omega_J+i\eta)\ . \tag{4}$$

Here H' and H are cell indices, $I=(c,k_i)$ is a conduction-band index, $J=(v,k_j)$ a valence-band index and N is the number of elementary cells (which will go to infinity, but is canceled if the remaining k summation is changed into integration). The corresponding expression for the elements of $\underline{\mathscr{K}}$ is

$$\begin{aligned}
\mathscr{K}_{H'H}(K,\omega)=N^{-1}\sum_{k_i,k_j,k_k,k_l}&\exp(ik_iH'-ik_kH)\delta_{k_i-k_j,K}\\
&\times\Bigg\{-V_{IJ'I'J}+G^{(S,T)}V_{IJ'JI'}\\
&+\sum_{A,B}P_AP_B\{[V_{IBAJ}V_{AJ'I'B}+G^{(S,T)}(2V_{BIAJ}V_{J'AI'B}-V_{BIAJ}V_{AJ'I'B}-V_{IBAJ}V_{J'AI'B})]n_A\bar{n}_B\\
&\quad\times(\omega-\omega_I-\omega_{I'}-\omega_B+\omega_J+\omega_{J'}+\omega_A+i\eta)^{-1}-V_{IJ'AB}(V_{ABI'J}-G^{(S,T)}V_{ABJI'})\\
&\quad\times[\bar{n}_A\bar{n}_B(\omega-\omega_A-\omega_B+\omega_J+\omega_{J'}+i\eta)^{-1}\\
&\qquad+n_An_B(\omega-\omega_I-\omega_{I'}+\omega_A+\omega_B+i\eta)^{-1}]\\
&\quad-(2V_{IAI'B}V_{BJ'AJ}-V_{IAI'B}V_{BJ'JA}-V_{IABI}V_{BJAJ}+G^{(S,T)}V_{IABI'}V_{BJ'JA})\\
&\quad\times[\bar{n}_An_B(\omega-\omega_I-\omega_A+\omega_B+\omega_{J'}+i\eta)^{-1}\\
&\qquad+n_A\bar{n}_B(\omega-\omega_{I'}-\omega_A+\omega_B+\omega_J+i\eta)^{-1}]\}\Bigg\}\ ,
\end{aligned}$$

where $I'=(c,k_k)$ and $J'=(v,k_l)$.

In the calculations several different levels of approximation have been employed.

(A) The irreducible vertex part $\underline{\mathscr{K}}$ has been truncated after the first-order term and unrenormalized one-particle Green's-function data have been used ($\omega_{\mathscr{I}}=\epsilon_{\mathscr{I}}$, $P_{\mathscr{I}}=1$).

(B) $\underline{\mathscr{K}}$ has been truncated after the first order again, and the $\omega_{\mathscr{I}}$ have been renormalized, but setting $P_{\mathscr{I}}=1$.

(C) $\underline{\mathscr{K}}$ has been truncated after the first order again, but both $\omega_{\mathscr{I}}$ and $P_{\mathscr{I}}$ have been renormalized (according to Table I).

(D) The complete second-order expression has been used for $\underline{\mathscr{K}}$ and unrenormalized one-particle Green's-function data have been used.

(E) The second-order expression has been used for $\underline{\mathscr{K}}$ again and both the $\omega_{\mathscr{I}}$ and $P_{\mathscr{I}}$ have been renormalized.

The results for the lower limit of the first exciton band obtained with these levels of approximation for the minimal and double-zeta basis sets are listed in Table II. Given are the excitation energy $E_{\rm ex}$ [the solution of Eq. (3)] and the binding energy of the exciton, defined as $E_{\rm bind}=E_{\rm gap}-E_{\rm ex}$, where $E_{\rm gap}$ is taken from Table I in the corresponding approximation (renormalized or unrenormalized). For renormalization we have always employed the second-order results of Table I.

One should observe that the excitation energy is de-

TABLE II. Lower limit of the first singlet exciton band of the bent HF chain. (All energies in eV.)

		A	B	C	D	E
MB[a]	E_{ex}	17.80	16.16	16.76	17.01	16.05
	E_{bind}	9.11	9.08	8.48	9.90	9.19
DZ[b]	E_{ex}	13.55	11.13	11.70	10.91	9.17
	E_{bind}	7.26	7.16	6.59	9.90	9.12

[a]Minimal basis (MB) set results.
[b]Double-zeta (DZ) basis set results.

creased by renormalization as well as by inclusion of second-order irreducible vertex parts. However, the exciton binding energy is not always increased simultaneously because the energy gap is considerably reduced by renormalization. This reduction is even larger than the reduction of E_{ex} by renormalization. Therefore, the exciton binding energy decreases in approximations B and C, with respect to approximation A. In addition, we note that E_{bind} also decreases when going from the incomplete renormalization (B) to the complete renormalization (C). This corresponds to the reduction of E_{ex} in C by taking into account the screening of the electron-hole interaction by polarization in C by the $P_{\mathscr{I}}$ factors.

In approximation D and E the excitation energy is again reduced with respect to A and C, respectively. In this case, however, the band gap is no more changed and the corrections give large contributions to the exciton binding energy, which therefore increases if we compare A to D and C to E. It is interesting to observe that, due to these compensation effects, approximation A gives the best exciton binding energies (compared to approximation E) among all approximations employing first-order irreducible vertex parts (A, B, and C).

IV. CONCLUSIONS

Our correlation calculations on the bent HF chain have led to an estimate of the ionization potential of solid HF lying about 1 eV below the ionization potential of the monomer. This is a pure correlation effect, largely due to third-order contributions in the case of the monomer.

For the first time it has been possible to include third-order self-energy diagrams and second-order irreducible vertex parts in *ab initio* Møller-Plesset calculations on a realistic system also containing nonhydrogen atoms. The trends observed in these calculations may be useful in selecting approximation schemes for more complex quasi-one-dimensional systems.

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