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Application of the Intermediate Exciton Formalism to H₂ Molecular Chains

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The interaction of the uncorrelated electrons and holes are taken into account in a model insulator of H₂ molecular chain by the use of the intermediate excitation theory. The calculations are performed at *ab initio* level showing that the correlation corrections to the forbidden energy gap are large.

Many electronic phenomena in chemistry and physics are correlational in nature. Much of the recent efforts in molecular quantum chemistry went into accounting for the correlation in ground and excited states using sophisticated and highly accurate *ab initio* Hamiltonians leading to theoretical calculations sometimes more accurate than experiments. In the field of solid state quantum calculations the situation is far from this perfection. Here heuristic correlational theories¹ stand without challenging real *ab initio* methods. This situation is understandable in the view of the fact that even Hartree-Fock (HF) calculations for solids are becoming widespread only recently. The difficulty is due to the extended nature of solids, the large (in principle infinite) number of interactions poses a difficulty not present in molecules. Furthermore, in solids, even in the restricted class of nonmetals where Hartree-Fock theory makes sense there are many more types of excitations than in a molecule².

According to our opinion, it is advantageous conceptually and even sometimes technically to make use of localized representation of the one electron orbitals in order to permit classification of configurations considered in the particular correlation calculations. Furthermore, direct space convergence can be numerically reasonably fast permitting an effective selection of terms. The need for such a transformation can be easily visualized considering a two-electron Coulomb integral in the delocalized (Bloch) or localized (Wannier) representation³. Let $\varphi_{nk}(r)$ be the Bloch orbital (BO) of the n -th energy band, with quasi-momentum k . The corresponding many-electron wavefunction is a Slater determinant for the ground state

* Festschrift of Professor Dušan Hadži.

$$\psi = [(Nm)!]^{-1/2} \det \left| \begin{array}{cccc} \varphi_{1k_1} (1) \alpha (1) & \varphi_{1k_1} (2) \beta (2) & \dots & \varphi_{k_N} \\ (2N) \beta (2N) & \dots & \varphi_m (2m N) & \beta (2m N) \end{array} \right| \quad (1)$$

with one-electron Bloch function (BF) in the LCAO form

$$\varphi_{nk} (r) = N^{-1/2} \sum_R \sum_{\alpha=1}^m e^{ikR} C_{n\alpha} (k) \chi_{\alpha} (r - R) \quad (2)$$

where R runs over cells, α over atomic orbitals $\chi_{\alpha} (r)$ within the unit cell and $C_{n\alpha} (k)$ are variational coefficients.

The Wannier functions (WF)

$$W_n (r - R) = \frac{1}{N} \sum_k^{\text{occ.}} \exp (-ikR) \varphi_{nk} (r) \quad (3)$$

are localized at the site R .

It is well known that where $N \cdot m \rightarrow \infty$

$$\langle nk, ml | 1/r_{12} | n' k', m' l' \rangle = \int \varphi_{nk} (r_1) \varphi_{ml} (r_2) \frac{e^2}{|r_1 - r_2|} \varphi_{n'k'} (r_1) \varphi_{m'l'} (r_2) d^3 r_1 d^3 r_2 \quad (4)$$

is of the order of $1/N$ while a similar integral over the WF-s of order of 1. This is a reason why configuration interaction (CI) is impossible in terms of BO-s. Since HF Bloch functions are becoming available for realistic systems these days, also their transformation to WF-s can be carried out. For the H_2 molecular chain studied here these WF-s have been already published earlier⁴.

In this communication we report on our calculations of the excitation energy of the most simple model insulator, the H_2 molecular chain at three different geometric arrangements. We shall make use of an *ab initio* Hamiltonian, i. e. all one-, two-, three-, and four-center integrals over atomic orbitals (AO) are calculated within a given range. Our AO basis consists of STO-3G functions⁵ each centered on the H atoms. The simplest approximation to the excitation energy is the difference of the lowest empty level and the highest occupied level,

$$\Delta E_k = \varepsilon_{LE} - \varepsilon_{HO} \quad (5)$$

according to the Koopmans' theorem⁶.

In a molecule several corrections are applicable to this, the simplest being (for singlets)

$$\Delta E = \Delta E_k - J + 2C \quad (6)$$

where J and C are the Coulomb and exchange integrals of the two orbitals involved in the excitation, respectively. This corresponds to a one configurational approximation and for extended systems

$$\Delta E - \Delta E_k \approx 1/N \quad (7)$$

However, the interaction of the electrons and holes represented by the molecular $-J + 2C$ term can be dealt with in the exciton theory using formally a very large (order of N) number of determinants.

If electrons and holes are allowed to interact, exciton bands will be formed⁷. Since we do not want to have a heuristic model for the excitons, neither the localized Frenkel nor the delocalized Wannier exciton picture is best here and some intermediate-coupling exciton formalism is needed. In principle one should carry out a CI calculation including as many as possible singly excited configurations. As is well known this can be done formally in the Bloch picture of the Wannier (localized) representation. Best is the mixed or exciton representation^{7,8} using basis functions of the following type (singlet case, spin indices dropped)

$$\Phi_{vc}(K, \beta) = N^{-1/2} \sum_k e^{i\beta k} \psi_{vc}(k - K \rightarrow k) = N^{-1/2} \sum_R e^{iKR} \psi_{vc}(R \rightarrow R + \beta) \quad (8)$$

v is for valence and c for conduction band.

Here K is the reciprocal wave vector of the exciton, the separation of the electron and hole. $\psi_{vc}(k - K \rightarrow k)$ refers to a singly excited one-determinant configuration with the $v, k - K \rightarrow c, k$ excitation in the Bloch representation, $\psi_{vc}(R \rightarrow R + \beta)$ is the $v, R \rightarrow c, R + \beta$ excitation in Wannier representation. $\beta \neq 0$ corresponds to charge-transfer (CT) states, which are to be included if we wish to go beyond the Frenkel excitons. It is essential to use this picture⁷ comprising N singly excited determinants of the $\psi_{vc}(k - K \rightarrow k)$ or $\psi_{vc}(R \rightarrow R + \beta)$ type because individual ψ_{vc} 's give merely corrections of the order of $1/N$ to the excitation energy. The excitation state of the many electron system may be approximated as

$$\psi^K = \sum_{\beta} U_K(\beta) \Phi_{vc}(K, \beta) \quad (9)$$

by limiting the discussion to singly excited configurations and to two bands only. After Takeuti⁸ we rewrite the Schrödinger equation for $U_K(\beta)$ in the following Green's function form

$$U_K(\beta) = \sum_{\beta'} \sum_{\beta''} G_K^E(\beta - \beta') V_K(\beta', \beta'') U_K(\beta'') \quad (10)$$

with the electron-hole pair Green's function

$$G_K^E(R) = N^{-1} \sum_k e^{ikR} \{ E - [\epsilon_c^{\text{HF}}(k) - \epsilon_v^{\text{HF}}(k - K)] \} \quad (11)$$

and electron-hole interaction (singlet case)

$$V_K(\beta, \beta') = \sum_R e^{iKR} [2 \langle c\beta, vR | vO, cR + \beta' \rangle - \langle c\beta, vR | cR + \beta' vO \rangle] \quad (12)$$

using notations similar to those of Knox⁷ ($c\beta$ stands for a conduction band Wannier function $w_c(r - \beta)$ centered at site β , etc.). Electron-electron integrals in (12) are to be evaluated over Wannier functions. This formalism has proven to be useful in the foundations of the exciton theories⁷. The first term in (12) is effectively the Coulomb interaction of two charge clouds $w_c(r - \beta) w_v(r)$ and $w_v(r - R) w_c(r - \beta')$ which does not decrease exponentially with R if $|\beta|$ and $|\beta'|$ are not too large. This does not lead, however, to any divergency in the summation over R , because both charge clouds have zero total charge due to the orthogonality of the Wannier functions⁷. The actual numerical convergence of this sum has been discussed recently in some

detail in connection with a semiempirical treatment of the excitation energy of polyacetylenes⁹. The integral evaluation has been carried out via the tedious AO to WF transformation in the way¹⁰ usual in molecular quantum chemistry. All other aspects of the numerical procedure are quite similar to the semiempirical calculations⁹.

The main results of the calculations are given in Table I. There are substantial differences between $\varepsilon_c(\pi/a) - \varepsilon_v(\pi/a)$ (the energy gap, E_g) and the exciton energies, showing a considerable electron-hole attraction. Since with decreasing R_2 the intermolecular interactions grow, the excitation energies (both E_g and the excitonic) diminish.

TABLE I
Excitation Energies from Crystal Orbital Approach and from CI Using Wannier Functions at $k = 0$

R_1	R_2	$E_g(k)$ $k = 0$	E_k	$E_g(k)$ $k = \pi/a$	Intermediate exciton (2-nd neighbour approximation)	Frenkel exciton (localized to one H_2 unit)
1.45	1.46	3.146		0.529	0.37	
1.45	1.9	2.507		0.677	0.49	0.535
1.45	4.35	1.399		1.123	0.92	
H_2^a			1.211 ^b			0.917

All values are in atomic units.

^a H_2 molecule $R = 1.45$ a. u.

^b Difference between molecular orbital energies.

In this calculations using the *ab initio* parameterless Hamiltonian we have demonstrated, that a substantial electronic correlation is to be expected during excitations of electrons in some insulators. Furthermore, the present calculations also demonstrate, that it is possible to carry out realistic correlation calculations for extended systems by the use of Wannier functions.¹¹ The application of these procedures to more realistic systems is largely restricted by the numerical time consuming evaluation of integrals over Wannier functions.

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IZVLEČEK

Uporaba formalizma vmesnih ekscitonov na molekulski verigi H_2 *Miklós Kertesz, Jože Koller in Andrej Ažman*

Standardni SCF računi ne upoštevajo korelacijske energije. Ker so spremembe energije, ki so največkrat deležne zanimanja, pogosto istega velikostnega reda kot korelacijska energija, je torej natančnost SCF računov premajhna. Molekule računamo po standardnem postopku, uporabimo namreč metodo konfiguracijske interakcije. Vzamemo čim več možnih konfiguracij ali pa izberemo tiste konfiguracije, katere največ doprinesejo k stanju, ki nas zanima. Za neskončne sisteme (eno- do tridimenzionalni kristali) takšni standardni postopki niso izdelani. V zadnjem času so se pojavili rutinski računi kristalnih orbital za enodimenzionalne neskončne sisteme. Energija ekscitacije je v grobem različna med energijo spodnjega roba prevodnega in zgornjega roba valenčnega pasu, če imamo opravka z izolatorjem ali polprevodnikom. Ta energija (imenujemo jo tudi širina energijske reže, E_g) je v večini primerov prevelika, ker ne upoštevamo korelacije. Metoda, ki bi bila podobna konfiguracijski interakciji, kot je uporabna pri molekulah, je tukaj težko izvedljiva. Veliko več je možnih tipov ekscitacij kot pri molekulah, pa tudi kristalne orbitale (Blochove funkcije) so delokalizirane funkcije. Pomagamo si na ta način, da transformiramo Blochove funkcije v lokalizirane Wannierove funkcije in uporabimo iz teorije trdne snovi znano teorijo ekscitonov. Ekscitonski nivoji se nahajajo med valenčnim in prevodnim pasom.

Opisan je račun na modelnem izolatorju, in sicer verigi H_2 molekul. Računi so bili izvršeni na ab-initio nivoju in so pokazali, da so korelacijski popravki k širini reže prepovedanih energij znatni.