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COMMENT

A comment on the charge excitation gap for polyacetylene

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Abstract. The charge excitation gap for polyacetylene $(\text{CH})_x$ was calculated using the Lanczos algorithm applied to small chains. The actual value of $4.5 \pm 0.4 \text{ eV}$ for this gap was obtained using the extended Hubbard model with the parameters fixed from *ab initio* calculations (reported elsewhere). For the second set of model Hamiltonian parameters recommended by many experimentalists (those measuring optical gaps or on-site spin densities in polyacetylene) the corresponding value for the charge transfer gap is $1.6 \pm 0.8 \text{ eV}$, which is reasonably close to what is considered the experimental value. Our results confirm the earlier finding that the electron correlations favour dimerization in polyacetylene.

1. Introduction

Energy band calculations for solids are difficult, costly and usual suffer from errors. The local density approximation [1,2] is successful in describing the ground-state properties of semiconductors and isolators, but the band gaps coming out of the calculations are frequently too small [3–5]. An alternative and much more costly approach, *ab initio* calculations performed in the Hartree–Fock approximation, yield band gaps that are too large [6–8]. Therefore, it becomes clear that in order to obtain correct values of the band gaps it is necessary to include electron correlation effects, i.e. all the effects of electron–electron interactions which are not included in the *ab initio* Hartree–Fock calculations. Unfortunately, such *ab initio* correlation calculations for infinite systems (and even for large molecules) are much more difficult, costly and time consuming, and only recently have such calculations become possible [7–11], which is a great achievement.

Ab initio correlation calculations for infinite one-dimensional polyacetylene that go beyond second-order perturbation expansion were reported in [12,13]. In these papers the dependence of the total ground-state energy on the dimerization was analysed. It was claimed that electron–lattice coupling alone leads only to a marginal dimerization of the chain and that the correlation effects are responsible for the observed large dimerization, as pointed out by Horsch about a decade ago [14]. A common model approach to the electron correlation problem in polyacetylene is an extension of the Su–Schrieffer–Heeger Hamiltonian [15,16], by the terms which describe the electron–electron interactions (the so-called Peierls–Hubbard Hamiltonian [17]). One of the significant results obtained by König and Stollhoff [13] was the mapping of their *ab initio* results onto the Peierls–Hubbard Hamiltonian [15,16]. In this way it was demonstrated that this model Hamiltonian contains the essential physics of the dimerization in polyacetylene.

If the electron–phonon coupling is neglected, the Peierls–Hubbard Hamiltonian reduces to the so-called extended Hubbard model [19] which has been studied by several authors.

The phase diagram of the extended Hubbard model was investigated using various techniques such, as Hartree–Fock [20], functional integral formalism [21], quantum Monte-Carlo [22], renormalization group and Lanczos method [23–25]. The ground state may correspond either to a free electron liquid, to a charge density wave, or to Mott–Hubbard states, depending on the precise values of the model parameters. Much less is known about the charge excitation gap of the one-dimensional extended Hubbard model for half-filling. It was discussed only in [23–25], with emphasis on a qualitative survey of the U – V plane in order to observe how the gap reflects itinerancy of the electrons.

The purpose of the present study is to answer an important question concerning the value of the charge excitation gap in polyacetylene when dimerization is present. We shall use exact diagonalization of finite systems and finite-size scaling to obtain the gap of a one-dimensional polyacetylene chain.

2. Computational details and results

We use the following Peierls–Hubbard Hamiltonian:

$$H = \sum_{i\sigma} t_{i,i+1} (c_{i\sigma}^\dagger c_{i+1\sigma} + c_{i+1\sigma}^\dagger c_{i\sigma}) + \sum_i U n_{i\uparrow} n_{i\downarrow} + \frac{1}{2} \sum_i V_{i,i+1} n_i n_{i+1} + 2NK\xi^2 + \mu \sum_i n_i \quad (2.1)$$

where i runs over all sites (all π orbitals), $t_{i,i+1} = t_0 \pm 2\alpha\xi$ are the hopping integrals, ξ is dimerization coordinate; N is the total number of sites (meaning C atoms) and α and K are the electron–phonon coupling and spring constants, respectively. In (1.1) $c_{i\sigma}^\dagger$ is the creation operator of a π electron with spin σ on site i , $n_{i\sigma}$ is the respective electron number operator and $n_i = n_{i\uparrow} + n_{i\downarrow}$; U is the on-site Coulomb repulsion of the electrons and $V_{i,i+1}$ is the nearest-neighbour Coulomb repulsion. As the effect of different length of the bonds on the value of $V_{i,i+1}$ is insignificant [13], we take $V_{i,i+1} = V$ in our calculations. For the half-filled band one has the chemical potential $\mu = U/2 + 2V$. The Hamiltonian (1.1) is invariant under particle–hole transformation. The same Hamiltonian (1.1) has been used by Loh and co-workers [17], and by Waas and co-workers [18] to study the ground-state properties of small clusters and to obtain the phase diagram depending on the parameters of the model.

Unfortunately, the values of the parameters entering the model Hamiltonian are not precisely known for polyacetylene. Here we use for most of them the values derived by König and Stollhoff from *ab initio* calculations. For the dimerization we take the experimental value $\xi = 2.6$ pm [26]. The fitted values of $t_0 = -2.5$ eV, $\alpha = 40$ meV pm⁻¹ give $t_{i,i+1} = t_0 - 2\alpha\xi = t_1 = -2.708$ eV for odd i , $t_{i,i+1} = t_0 + 2\alpha\xi = t_2 = -2.292$ eV for even i ; electron–electron interactions are described by $U = 11.5$ eV, $V = 2.4$ eV [13].

The very large value of U ($U > -4.0t_0$) entering this set of model parameters is not universally accepted as the correct one. Many experimentalists and theoreticians favour a much lower value: $-1.5t_0 < U < -3.5t_0$ [27–30]. (There is less agreement about V . Some authors [28, 29] suggest that: $-0.5t_0 < V < -1.5t_0$). Therefore, in the following, we will also consider the second set of model Hamiltonian parameters: $U = -2.5t_0 = 6.25$ eV [28–30] and $V = U/2 = 3.125$ eV. Note that the value of V equal to one half of U corresponds roughly to maximal possible dimerization, as found in small cluster calculations [18]. For

the sake of simplicity, the remaining parameters entering both sets are taken to be exactly the same.

The Lanczos method is an excellent one to obtain low-lying eigenvalues for a small cluster. As the method is described in detail in numerous papers and textbooks (see, for example, [31, 32] and [17, 18, 23–25]), we will not repeat here its description. For small clusters of $N = 6, 8, 10, 12$ sites the actual computations were fast and could be completed on personal computers or small workstations.

We have used both modified cyclic (periodic) (MPBC) and free boundary (FBC) conditions. The importance of imposing the proper boundary conditions in small cluster calculations was recognized by several authors [18, 33, 34]. Namely, there is a subtle difference between the chains with $N = 4m$ and $N = 4m + 2$ sites, respectively, known also in quantum chemistry. In order to approximate the infinite chain by finite rings with the states at the Fermi level, the cyclic boundary conditions are the most suitable in the first case, whereas the anticyclic boundary conditions have to be taken in the second one. A more detailed discussion is given in the appendix. For calculations with anticyclic boundary conditions we used $t_{N,N+1} = t_{N,1} = -t_2$, which corresponds to $c_{N+1,\sigma} = -c_{1,\sigma}$ and for both types of boundary conditions $V_{N,N+1} = V_{N,1} = V$ was assumed.

For free boundary conditions one has $V_{N,N+1} = 0$ and $t_{N,N+1} = 0$. The elastic energy term in (1.1) should be modified to $2(N - 1)K\xi^2$. Furthermore, it is clear that any results for small clusters will be different for two different choices; namely, we can take either $t_{i,i+1} = t_1$ and $t_{j,j+1} = t_2$, as described above for the closed rings where i and j are odd and even numbers respectively, or $t_{i,i+1} = t_2$ and $t_{j,j+1} = t_1$. In order to minimize the effect of free boundaries it is necessary to perform all the computations for each of the two above-mentioned cases separately, and take the average value of the energy obtained in each case as a final result. Note that for cyclic and anticyclic boundary conditions such a problem does not exist. We have verified in our calculations that the results obtained are independent of the chosen value of the last hopping element in (1.1), being either $-t_1$ or $-t_2$.

The charge excitation gap for small- N site clusters, E_{gap}^N , according to the well known formula [23–25, 35] is given by

$$E_{\text{gap}}^N = E_0^N(n_{\uparrow}, n_{\downarrow} + 1) - 2E_0^N(n_{\uparrow}, n_{\downarrow}) + E_0^N(n_{\uparrow}, n_{\downarrow} - 1) \quad (2.2)$$

where $E_0^N(n_{\uparrow}, n_{\downarrow})$ is the ground-state energy of the N site system with n_{\uparrow} and n_{\downarrow} electrons for $\sigma = \uparrow$ and \downarrow , respectively. We consider here the half-filled case $n_{\uparrow} = n_{\downarrow} = N/2$. Furthermore, thanks to the particle-hole symmetry it is sufficient to calculate only $E_0^N(\frac{1}{2}N, \frac{1}{2}N)$ and $E_0^N(\frac{1}{2}N, \frac{1}{2}N + 1) = E_0^N(\frac{1}{2}N, \frac{1}{2}N - 1)$ [23–25, 35] to calculate E_{gap}^N from (2.2). Note, however, that it is not true for FBC and for the dimerized case (i.e. for $t_1 \neq t_2 \neq t_0$) where the particle-hole symmetry breaks down.

The charge excitation gap, E_{gap}^N , was calculated for clusters of $N = 6, 8, 10$ and 12 , for both types, MPBC and FBC, of the boundary conditions, and for the dimerized ($t_1 = -2.708$ eV, $t_2 = -2.292$ eV) as well as the non-dimerized ($t_1 = t_2 = -2.5$ eV) case and for two sets of model Hamiltonian parameters U and V , i.e. $U = 11.5$ eV, $V = 2.4$ eV [13] and for $U = 6.25$ eV, $V = 3.125$ eV [28–30].

Before the presentation of the data let us make a technical remark. Namely, prior to any calculations the question about the precise values of model parameters has to be addressed. The problem of the correct choice of the values of t_0 , U , V has been already discussed. However, there are also some doubts about the precise values of α and K . Thus in order to proceed further we have to make some assumptions. We have chosen to

use $\alpha = 40 \text{ meV pm}^{-1}$ as obtained in [13] and the experimental value of the dimerization $\xi = 2.6 \text{ pm}$ [26]. The value of K was next fixed by demanding that the total energy E_0 , as a function of dimerization parameter ξ has an absolute minimum exactly at $\xi = 2.6 \text{ pm}$. The technical implementation of these ideas is as follows. We compute $\mathcal{E}_0^N(\frac{1}{2}N, \frac{1}{2}N, K = 0|\xi) = E_0^N(\frac{1}{2}N, \frac{1}{2}N, K = 0|\xi)/N$: the minimal energy per site of the N -site Hamiltonian (1.1) with K fixed to zero for $N = 6, 8, 10, 12$ and for $\xi = 0, 1.5, 3.0$ and 4.5 pm . For each one of the fixed ξ we make extrapolation to obtain $\mathcal{E}_0^\infty(K = 0|\xi)$: the minimal energy per site for the infinite chain (at half-filling), using $N = 6, 8, 10, 12$ data points. As an example, we assume (compare [17, 18, 23–25, 36]) that $\mathcal{E}_0^\infty(K = 0|\xi) \approx e_1 + e_2/N$. The value e_1 is the extrapolated minimal energy we were looking for (in the limit of $N \rightarrow \infty$): $e_1 = E_0^\infty(K = 0|\xi)$. Next, we take four such values: $E_0^\infty(K = 0|\xi_j)$ for $\xi_1 = 0, \xi_2 = 1.5 \text{ pm}, \xi_3 = 3.0 \text{ pm}$ and $\xi_4 = 4.5 \text{ pm}$ and fit them with a parabola $\mathcal{E}_0^\infty(K = 0|\xi) = a + b\xi + c\xi^2$. Finally, with a, b and c at our disposal we find that $K = 2.543 \text{ meV pm}^{-2}$ for the first set of t_0, U, V (i.e. for $-2.5 \text{ eV}, 11.2 \text{ eV}$ and 2.4 eV , respectively). For the second set (i.e. for $-2.5 \text{ eV}, 6.25 \text{ eV}$ and 3.125 eV) we obtained $K = 3.132 \text{ meV pm}^{-2}$. These values will be used for all our subsequent computations. One may, of course, object that such a procedure of first making an extrapolation to $N = \infty$ and subsequently fitting the extrapolated data is likely to yield some errors. To address this problem we repeated all the above-mentioned calculations using the raw data for the largest cluster ($N = 12$) instead of making an extrapolation. The values of K obtained that way are very close to our primary choice. This simple consistency test gives some additional support to the K values which we use in what follows.

With the values of all the parameters fixed the question arises of how to extrapolate small cluster results for E_{gap} to an infinite system. It is well known [23–25, 36] that E_{gap} is roughly linear with $1/N$ so the extrapolation to infinite system is again possible. In fact, for all cases all four data points for E_{gap} against $1/N = 1/6, 1/8, 1/10, 1/12$ fit nicely onto a straight line. We do not feel that the cubic Legendre extrapolation (compare [23]), or a parabolic one, would be a better choice. There is a danger of obtaining an error being due to the so-called Runge phenomena for polynomial interpolation [28]. (In fact, for unnatural, so-called modified antiperiodic boundary conditions [23], such an error was indeed identified when trying cubic Legendre interpolation). Our method agrees as well with the extrapolation performed by Waas and co-workers [18] for the dimerization parameter.

The final results for the first set of model Hamiltonian parameters ($t_0 = -2.5 \text{ eV}, U = 11.5 \text{ eV}, V = 2.4 \text{ eV}, K = 2.543 \text{ meV pm}^{-2}$) are presented in figure 1. One finds the gap of $E_{\text{gap}} = 4.5 \text{ eV}$ for the modified periodic boundary conditions. In figure 2 we present similar results obtained for the free boundary conditions, which gave $E_{\text{gap}} = 4.1 \text{ eV}$. They are not too reliable, as the finite-size effects are definitely much more pronounced in small clusters with free boundary conditions. Nevertheless, the relatively small discrepancy of 0.4 eV from our previous result can serve as an estimate of the error in the obtained value of E_{gap} . Thus our final result is $E_{\text{gap}} = 4.5 \pm 0.4 \text{ eV}$. This value should be compared to an approximate 4.3 eV value mentioned in [13] which was obtained using the model (1.1) with a different value of $K = 3.9 \text{ meV pm}^{-2}$. There are two possible reasons for the small discrepancy found. First, it may be caused by an approximate treatment of local correlation within the local approach ansatz [7–10] with a small subset of local operators [8]. Second, it seems that the value of K , found in [13] from the self-consistent field calculation, has to be reduced when electron correlation effects are taken into account.

For the second set of the model Hamiltonian parameters ($t_0 = -2.5 \text{ eV}, U = 6.25 \text{ eV}, V = 3.125 \text{ eV}, K = 3.132 \text{ meV pm}^{-2}$) the corresponding results for the modified periodic boundary conditions are presented in figure 3 and the results for the free boundary conditions

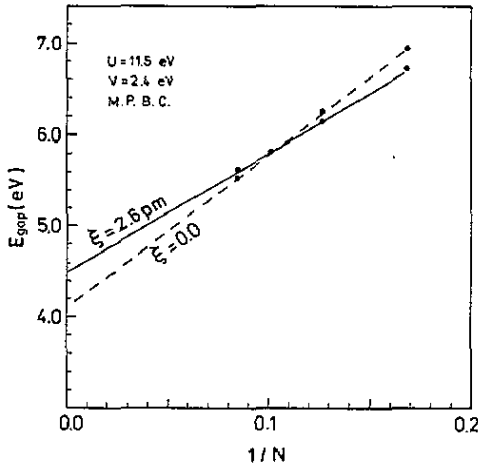


Figure 1. Charge excitation gap, E_{gap}^N , calculated with the modified periodic boundary conditions (MPBC) as a function of $1/N$. Results of finite cluster calculations are given by dots. The full curve corresponds to the dimerized case ($\xi = 2.6$ pm), the broken curve to the non-dimerized one ($\xi = 0$) ($t_0 = -2.5$ eV, $U = 11.5$ eV, $V = 2.4$ eV).

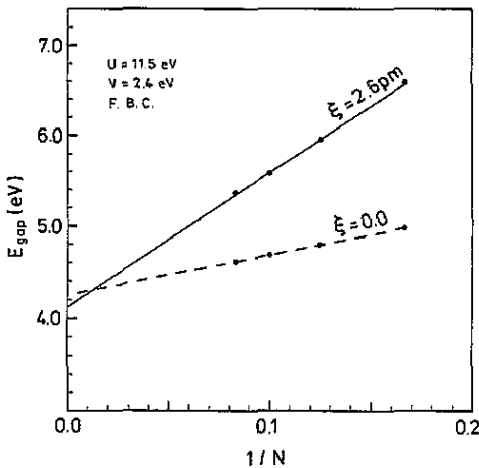


Figure 2. Charge excitation gap, E_{gap}^N , calculated with the free boundary conditions (FBC) as a function of $1/N$ ($t_0 = -2.5$ eV, $U = 11.5$ eV, $V = 2.4$ eV). The meaning of the data points and curves are as in figure 1.

in figure 4. The charge transfer gap in this case is $E_{\text{gap}} = (1.6 \pm 0.8)$ eV, which is reasonably close to the experimental values 1.8–1.9 eV [27–29, 36]. Thus our result supports the second set of parameters, namely the one with smaller U/t_0 .

3. Summary and conclusions

The results of our calculations confirm the earlier findings [14, 17, 18, 23] and demonstrate

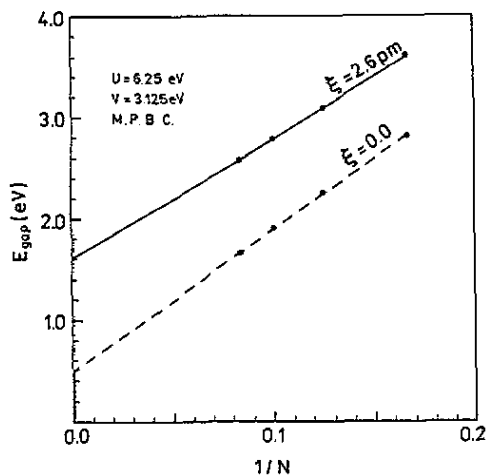


Figure 3. Charge excitation gap, E_{gap}^N , calculated with the MPBC as a function of $1/N$ ($t_0 = -2.5 \text{ eV}$, $U = 6.25 \text{ eV}$, $V = 3.125 \text{ eV}$). The meaning of the data points and curves are as in figure 1.

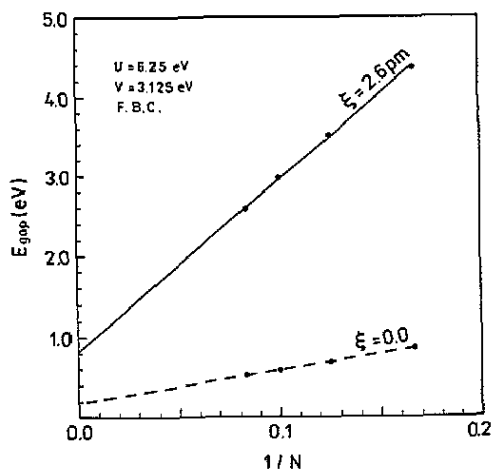


Figure 4. Charge excitation gap, E_{gap}^N , calculated with the FBC as a function of $1/N$ ($t_0 = -2.5 \text{ eV}$, $U = 6.25 \text{ eV}$, $V = 3.125 \text{ eV}$). The meaning of the data points and curves are as in figure 1.

that the correlation effects indeed favour dimerization in polyacetylene. We have found that for all clusters the ground-state energy of dimerized state is lower than the one obtained for the non-dimerized state.

The performed diagonalization of finite clusters shows that the dimerization makes E_{gap} (2.3) larger with respect to the non-dimerized case.

Finally, for the first set of model Hamiltonian parameters (characterized by a large value of U/t_0) we obtained $E_{\text{gap}} = 4.5 \pm 0.4 \text{ eV}$. For the second set (with small U/t_0) we obtained $E_{\text{gap}} = (1.6 \pm 0.8) \text{ eV}$ which is very close to the experimental result. The controversy over

which model is correct (the one with the larger or the smaller U/t_0) cannot, however, be settled with these results. There is a possibility that the model Hamiltonian is too simple to describe correctly both the dimerization and the gap and therefore it might be necessary to take into account long-range Coulomb interactions (instead of a single nearest-neighbour V -term) [28, 39].

Finally, we would like to stress the many-body character of the ground state found in the exact diagonalization of finite clusters. For both sets of model Hamiltonian parameters this many-body character is inherent in the formation of the gap in the electronic states of polyacetylene. Therefore, the value of this gap cannot be quantitatively explained by the band structure calculations performed within the local density approximation [38].

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Appendix

For the half-filled band in the free-fermion case ($U = V = 0$) the Fermi momentum of the infinite chain is $|k_F| = \frac{1}{2}\pi$ [18,34]. For small systems one would then expect better extrapolated results to the infinite chain if $|k_F| = \frac{1}{2}\pi$ was included in the set of individual momenta, k_j . Applying periodic boundary conditions the allowed wave vectors k_j are $k_j = 2\pi j/N$ and the above condition is fulfilled only for $N = 4n$. If we use antiperiodic boundary conditions [18,29,34], the allowed wave vectors are $k_j = 2\pi j/N + \pi/N$, and $|k_F| = \frac{1}{2}\pi$ is included instead for $N = 4n + 2$. This procedure eliminates undesired oscillations of the calculated energies. With increasing N the dependence on N vanishes.

Antiperiodic boundary conditions are equivalent to a transformation of fermion operators as follows: $c_{N+1,\sigma} = -c_{1,\sigma}$ and $c_{i,\sigma} = c_{i,\sigma}$ for $i \leq N$. This transformation changes the sign of the hopping element $t_{N,1}$, which closes the ring, and leaves the on-site and inter-site Coulomb interactions invariant. Therefore the antiperiodic boundary conditions can be easily implemented in the real space calculations for the chains of $N = 4n + 2$ atoms described by the Hamiltonian (1.1) by taking the terminal hopping element with the reversed sign.

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