Calculation of the electronic structure of organic polymers as solids

János J. Ladik

Institute for Theoretical Chemistry and Laboratory of the National Foundation
for Cancer Research at the Friedrich-Alexander-University Erlangen-Nürnberg
Egerlandstr. 3, D-8520 Erlangen, FRG

Abstract – The paper advocates the application of a mixture of theoretical
molecular physical – a solid state physical quantum mechanical methods to
treat the electronic structure and solid state physical properties of poly-
mers. The latter ones are the really important properties which determine
their applicability as plastics and as new types of materials as well as
the functions of biopolymers.

After a brief sketch of the Hartree-Fock crystal orbital theory to
calculate the energy band structures of periodic polymers, methods for the
treatment of non-periodic polymers and their electron-correlation problem
are outlined. Techniques to compute interactions between them and to take
into account the effect of environment on their band structures are briefly
mentioned.

Finally, the paper gives a short discussion of the results for the elec-
tronic structure of a few illustrative examples.

1. INTRODUCTION

Organic polymers play a very important role in chemistry, biology and solid state physics.
They form plastics, like PVC, teflon, polyacrilnitril etc., they play a key role in life
processes, like DNA, RNA, proteins, polysaccharides etc. and finally, due to their com-
plexity they give possibilities for unusual physical phenomena, like the occurrence of
solitons in DNA and proteins, polymeric superlattices in copolymers, different highly con-
ducting polymers (doped $(CH)_x$, $(SN)_x$), the TCNQ-TTF system doped poly-p-phenylenes etc.)
After the discovery of low T_c superconductivity also in some polymers (SN_x, the Se analogue
of tetratiofulvalene stack) and most recently finding high T_c superconductors in ceramics
(the $La_{2-y}Ba_yCuO_4-$ (ref. 1) and $YBa_2Cu_3O_{7-\delta}$ (ref. 2) crystals) rather probably also
high T_c superconducting polymeric systems will be discovered.

Though polymers are not necessarily quasi one-dimensional, most of them are. One the other
hand besides some periodic polymers (like polyethylene, teflon, $(SN)_x$, etc.) most of them
are not periodic at all (proteins, DNA, many copolymers or any kinds of doped polymers).

To understand the different chemical and physical properties of polymers and espeicially to be
able to predict some technologically useful polymers (as coating materials, prospective
elements of new kinds of chips, materials used to new kind of lattices, solar cells and non-
linear optical devices, etc.) as well as the biological functions of biological macromolecules
one has to be able to treat accurately enough their electronic structure. Only in this way
it will be possible to take advantage of the complex solid state physical nature of poly-
mers and synthetize "taylor made" polymers for different technological or biological purposes.

To understand the non-local solid state physical properties of polymers (charge and energy
transport, plasmons and solitons in polymers, their excitonic and phonon spectra, magnetic
and mechanical properties, etc.) one has to take into account that each polymer (independently
whether it is an insulator, semiconductor or conductor) is a rather complicated solid usu-
ally with a larger number of atoms (orbitals) in its unit cell. Therefore it is not enough
to treat its constituent molecules or residues with the help of quantum chemical methods,
but one has to merge the methods of molecular physics with those of theoretical solid state
physics.

If the polymer is periodic one can use the extension of the <u>Hartree-Fock-Roothaan</u> equations
(ref. 3) to solids (ref. 4) to obtain its <u>energy band structure. If the polymer is non</u>-
periodic different methods (see below) of <u>the theory of disordered systems</u> can be applied
to obtain the energy level distribution [density of states (DOS) curves of the polymer]
Since the Hartree-Fock band structure calculation always gives a too large fundamental gap
in any solid, one has to correct not only the total energy per unit cell, but also at least
the position of the valence (highest filled) and conduction (lowest unfilled) bands for

correlation (one obtains in this way a so-called quasi-particle (QP) band structure) which has an essentially smaller gap in reasonable agreement with experiment (see also below). Finally, to be able to treat any kind of physical properties of any kind of polymer, one has to be able to handle both the interaction between polymeric chains and the effect of the environment on the electronic structure of a polymer (the latter is especially important in the case of biopolymers). Both problems have been already solved in a satisfactory way.

Computer programs for all these methods are available on different computers and supercomputers. This means that in addition to the excitonic and vibrational spectra of some polymers with a smaller unit cell, we are now in the position to calculate any kind of physical property of any type of polymer.

2. METHODS

2.1. Hartree–Fock–Roothaan equations for quasi 1D solids

One can write down the crystal orbital (CO) of a quasi 1D solid(polymer) as a linear combination of Bloch orbitals (ref. 4).

$$\Psi(k,\vec{r})_\lambda = \sum_{g=1}^{m} C(k)_g \, \varphi(k,\vec{r})_g \tag{1}$$

where the Bloch orbital $\varphi(k,r)_g$ can be defined in its LCAO form as

$$\varphi(k,\vec{r})_g = \sum_{q=-N}^{N} \frac{1}{\sqrt{2N+1}} \, e^{ikqa} \, \chi_g^q \tag{2}$$

Here k is the crystal momentum, 2N+1 denotes the number of unit cells, a the elementary translation, χ_g^q the g-th AO centered in the q-th unit cell. If one applies the Ritz variational procedure, takes into account the translational symmetry and introduces the Born-Kármán periodic boundary conditions (the polymer is not taken as an open chain, but as a loop),introduces the Fock operator $\hat{F}$ as the one-electron operator, one arrives after some algebra to the expression of the ab initio SCF LCAO CO theory (ref. 4)

$$\underline{F}(k)\,\underline{C}_\lambda(k) = \mathcal{E}_\lambda(k)\,\underline{\underline{S}}(k)\,\underline{C}(k) \tag{3}$$

$$\underline{F}(k) = \sum_{q=-\infty}^{\infty} e^{ikqa}\,\underline{F}(q) \,, \quad \underline{\underline{S}}(k) = \sum_{q=-\infty}^{\infty} e^{ikqa}\,\underline{\underline{S}}(q) \tag{4}$$

with the matrix elements

$$\left[\underline{\underline{S}}(q)\right]_{r,s} = \left\langle \chi_r^o \,\middle|\, \chi_s^q \right\rangle \tag{5a}$$

and

$$\left[\underline{F}(q)\right]_{r,s} = \left\langle \chi_r^o \,\middle|\, -\tfrac{1}{2}\Delta - \sum_{t=1}^{M} \frac{Z_t}{|\vec{r}-\vec{R}_t^q|} \,\middle|\, \chi_s^q \right\rangle +$$
$$+ \sum_{u,v} P_{u,v}(q_1-q_2) \left(\left\langle \chi_r^o(1)\,\chi_u^{q_1}(2)\,\middle|\, \tfrac{1}{r_{12}}(1-\tfrac{1}{2}\hat{P}_{1\to2})\,\middle|\, \chi_s^q(1)\,\chi_v^{q_2}(2)\right\rangle\!\right) \tag{5b}$$

Here the subscripts in the AO-s χ specify always which AO has to be considered and the superscript q gives the unit cell in which it is centered, z_t is the nuclear charge of atom t (M is the number of atoms in the unit cell) and the vector $\vec{R}_t^q$ gives the position of atom t in cell q. In the two-electron part of (5b) the operator $\hat{P}_{1\to2}$ exchanges the coordinates of electron 1 and 2, respectively on the r.h.s. from this operator and finally the charge-bond order matrix elements $P_{u,v}(q_1-q_2)$ are defined in the quasi 1D case as

$$P_{u,v}(q_1-q_2) = \frac{a}{\pi} \sum_{\lambda=1}^{n^*} \int_{-\pi/a}^{\pi/a} e^{ik(q_1-q_2)} C_{\lambda,\mu}^*(k)\,C_{\lambda,v}(k)\,dk \tag{6}$$

(n^* is the number of filled bands).

Equ.-s (3) and (6) define a complete ab initio procedure which makes it possible to calculate the band structure of any periodic polymer including those which possess instead of a simple translation a combined symmetry operation (for instance in the case of a helix a screw operation (translation + rotation)). In this case the crystal momentum k is defined on the combined symmetry (ref. 5).

Another important question is, how many neighbors one has to take into account in the Fourier transforms (4) to obtain consistent results. Suhai (ref. 6) who has investigated this problem in detail came to the conclusion that if one does not want to destroy the periodic symmetry of the polymer and wants to take care of the conservation of its electric neutrality, one has to apply different cut-off radii for the different kinds of integrals occurring in equ.-s (5a) and (5b).

2.2. Non-periodic polymers

In the general case of a disordered system the coherent potential approximation (CPA) with an energy and k-dpendent self-energy seems to be the relatively most accurate method to obtain the DOS of the system (ref. 7). On the other hand if one has a quasi 1D system one can obtain the DOS-s of a non-periodic polymer much more easily and accurately using the negative factor counting (NFC) technique (ref. 8) based on Dean's negative eigenvalue theorem (ref. 9).

To summarize the NFC method let us assume that we have in a quasi 1D chain N units and 1 oribtal per unit (Hückel approximation). (Of course we can obtain in this way the DOS of only one band, for instance the valence band of a multicomponent system.) The resulting Hückel determinant will be tridiagonal (in the first neighbors' interactions approximation),

$$
\left| \underline{\underline{H}}(\lambda) \right| =
\begin{vmatrix}
\alpha_1 - \lambda & \beta_2 & 0 & 0 & \cdots\cdots & 0 \\
\beta_2 & \alpha_2 - \lambda & \beta_3 & & & \\
0 & \beta_3 & \alpha_3 - \lambda & \beta_4 & & \\
\vdots & & & & & \\
& & & & & \\
0 & & & & \beta_N & \alpha_N - \lambda
\end{vmatrix}
= 0 \qquad (7)
$$

where N is a large number ($N = 10^3$ or even 10^4). After performing a band structure calculation by taking all the components periodically repeated, the diagonal elements α_i and the off-diagonal ones β_j can be determined on the basis of the position of the band under consideration in the periodic case of the appropriate component and taking into account the band widths (ref. 8).

If we could find out all the roots of (7), we could write

$$
\left| \underline{\underline{H}}(\lambda) \right| = \prod_i^N (\lambda_i - \lambda) \qquad (8)
$$

Since this is not generally the case (or would require astronomic computer times) instead of this one can bring the tridiagonal determinant into a didiagonal form by wiping out the lower diagonal using a Gaussian elimination technique. (To start this procedure one has to substract from the second row of the determinant the first one multiplied by $\beta_2 (\alpha_1 - \lambda)$. Denoting the new diagonal elements of the didiagonal equivalent of (7) by $\varepsilon_i(\lambda)$, we can write

$$
\left| \underline{\underline{H}}(\lambda) \right| = \prod_{i=1}^N \varepsilon_i(\lambda) \qquad (9)
$$

where $\varepsilon_i(\lambda)$ can be calculated for a chosen value of λ very quickly with the help of the recursion formula

$$
\varepsilon_i(\lambda) = \alpha_1 - \lambda - \beta_i^2 / \varepsilon_{i-1}(\lambda) \qquad i = 2,3,4 \qquad (10)
$$
$$
\varepsilon_1(\lambda) = \alpha_1 - \lambda
$$

Comparing equ.-s (8) and (9), it is easy to see that for a given λ-value the number of eigenvalues smaller than λ ($\lambda_i < \lambda$) has to be equal to the number of negative $\varepsilon_i(\lambda)$ factors.

By giving λ different values throughout the spectrum and taking the difference of the number of negative $\varepsilon_i(\lambda)$-s belonging to consecutive λ-values, one can obtain a histogram for the distribution of eigenvalues (density of states) of $\underline{\underline{H}}$ for any desired accuracy.

One should mention that the method works not only in the one-band case, but one can obtain in a similar way the total DOS curves of a multicomponent disordered system, with the corresponding Fock and overlap matrix blocks (ref. 10). For instance if one has a unit B after unit an A the matrix blocks $\begin{pmatrix} \underline{F}^{AA} & \underline{F}^{AB} \\ \underline{F}^{BA} & \underline{F}^{BB} \end{pmatrix}$ have to be computed (ref. 10).

2.3. Correlation in polymeric chains

For an infinite or finite but long polymeric chain only size-consistent methods can be used
to treat the electron correlation problem. Until now the Moeller-Plesset (MP) (ref. 11) many
body perturbation theory has been applied for polymers in the second (ref. 12) and in a few
cases in the third order (ref. 13) to correct the total energy per unit cell as well as the
valence- and conduction bands (quasi-particle (QP) band structures).

In the MP theory one partitiones the total Hamiltonian in the form

$$\hat{H} = \hat{H}_o + \hat{H}' = n\,\hat{F} + \hat{H}'$$ (11)

where n is the number of electrons and $\hat{H}'$ is the deviation from the sum of the Fock operators.
One can show that the first order perturbation energy is already included in the E_{HF}
(Hartree–Fock energy) and for the second order one can derive for an infinite system in its
ground state the expression (ref. 12)

$$E_2^{(N)} = \sum_{I,J,A,B} \frac{\left|\left\langle \varphi_I(1)\,\varphi_J(2)\left|\frac{1}{r_{12}}(1-\hat{P}_{1\to 2})\right|\varphi_A(1)\,\varphi_B(2)\right\rangle\right|^2}{\mathcal{E}_I + \mathcal{E}_J - \mathcal{E}_A - \mathcal{E}_B}$$ (12)

where the combined index I stands for the band index n_i and k-value k_i. The $\mathcal{E}$-s in the
denominator are one particle energies (in an infinite system the Coulomb- and exchange
integrals occurring in the HF singlet excitation energy expression vanish (ref. 14))

One can write (12) in the simpler form

$$E_2 = \sum_{I,J} \mathcal{E}_{I,J} \quad ; \quad \mathcal{E}_{I,J} = \sum_{A,B} \frac{\left|\left\langle \varphi_I\,\varphi_J\left|\frac{1}{r_{12}}(1-\hat{P}_{12})\right|\varphi_A\,\varphi_B\right\rangle\right|^2}{\mathcal{E}_I + \mathcal{E}_J - \mathcal{E}_A - \mathcal{E}_B}$$ (13)

One can express E_2 in a similar way as a sum of pair correlation energies also if there
is an extra electron in the conduction band (N+1 electron system) or a positive hole in
the valence band (N-1 system). Knowing that

$$\mathcal{E}_c^{k_c}(QP) = E^{(N+1)} - E^{(N)}$$ (14a)

$$\mathcal{E}_v^{k_v}(QP) = E^{(N)} - E^{(N-1)}$$ (14b)

(generalized Koopmans' theorem) and substituting for $E^{(N+1)}$, $E^{(N)}$ and $E^{(N-1)}$ the expressions
E(HF) + E_2 (where E_2 is the MP/2 correlation energy) one can finally write (ref. 12)

$$\mathcal{E}_c(QP) = \mathcal{E}_c(HF) + \sum_c^{(N+1)}(e) + \sum_c^{(N+1)}(h)$$ (15a)

$$\mathcal{E}_v(QP) = \mathcal{E}_v(HF) + \sum_v^{(N)}(e) + \sum_v^{(N)}(h)$$ (15b)

The four self-energies occurring in equ.-s (15a) and (15b) can be easily expressed as the
difference of the appropriate sums of the pair correlation energies $E_{I,J}^{(X)}$ (X = N-1, N, N+1)
(ref. 12). One can define in a similar way quasi particle band structures using MP/3
(ref. 13). The calculation of QB band structures using the coupled cluster theory (ref. 14)
in the $1 + \hat{T}_2 + \frac{1}{2}\hat{T}_2\hat{T}_2$ approximation is in progress (ref. 15).

2.4. Interaction between polymer chains and the effect of environment

If one has a larger number of interacting molecules or differnt interacting chains at medium
distances 2.6 r 4.0 A one cannot afford the supermolecule (superchain) approach and a per-
turbational theoretical treatment of the interacting systems is both rather inaccurate and
very complicated. With the help of a new method, developed in Erlangen, the problem still
can be solved in a satisfactory way. One can solve the HF problem of a molecule or a chain
in the presence of all the others

$$\widetilde{F}^A\widetilde{\varphi}_i^A = \left(\hat{F}^A + \sum_{I\neq A} V^I(\varrho_I)\right)\widetilde{\varphi}_i^A$$ (16a)

$$\widetilde{\widetilde{F}}^B\widetilde{\varphi}_i^B = \left(\hat{F}^B + \widetilde{V}^A(\widetilde{\varrho}_A) + \sum_{I\neq A,B} V^I(\varrho_I)\right)\widetilde{\varphi}_i^B$$ (16b)

for all the interacting systems. In each iteration step the density

$$\rho_I(\vec{r}) = \sum_{i=1}^{m^*} \varphi_{i,I}^*(\vec{r}) \, \varphi_{i,I}(\vec{r}) \tag{17}$$

will change and with it also the potential $V^I(\mathcal{S}_T)$ of system I. One can go around all sub-systems until a mutually consistent (MCF) solution is reached which happens usually in a few iteration cycles (ref. 16). The real difficult problem was the proper representation of the potentials V^I of the subsystem with the help of point charges. One wanted on the one hand accurate enough interaction energies (which automatically contain besides the electrostatic also the polarization contribution) and which can be supplemented in a simple way by the exchange and charge transfer terms (ref. 17) and on the other hand a rather fast method. The dispersion interaction energies can still be added using London's empirical expression (ref. 18).

This method was successfully applied also to calculate the simultaneous interaction of more than hundred water molecules around a cytosine stack to generate a mean field acting on the stack (ref. 19).

3. SHORT DISCUSSION OF SOME SELECTED RESULTS

Using the ab initio SCF LCAO CO method a large number of calculations have been performed for different selected polymers. For poly(H-F) the different forms of polyacetylene, for polyethylene, for polyfluoroethylene and for $(SN)_x$ also different basis sets have been applied. We do not give here all the appropriate references, but refer to Chapter 2 of the book mentioned in ref. 4. With a minimal basis set the calculations have been extended also to systems with larger unit cells like polypyrrole, polythiophene and its derivatives as well as to the four nucleotide base stacks, for 3 polynucleotides (X+S+P, where X stands for C,T or A, S for the sugar and P for the phosphate group) and for all the 20 homopolypeptides (when the same 20 amino acid residue is repeated).

One could find – in agreement with chemical intuition – that if one calculates the band structures of a covalently bound chain (like polyacetylene or polyethylene) both the valence and conduction bands become very broad (4-6 eV). If one deals with a stacked system (TCNQ-TTF and the nucleotide base stacks) the widths of these bands are between 0.1 and 1.0 eV. Since the TCNQ-TTF charge transfer system is a good conductor, one would expect that a nucleotide base stack which has similar band widths if it is periodic (the same base is repeated) would become also a rather good conductor if it could be successfully doped with an electron donor or acceptor (which is not a trivial task). Finally, if a chain is held together only by hydrogen bridges (H-F...H-F...) we have found that the band widths are below 0.1 eV.

In the case of non-periodic polymers we have checked the matrix block NFC method by calculating the DOS of an alternating glyala chain. Since in this case also a direct band structure calculation could be performed, one could compare the DOS curves obtained in the two different ways (see Chapter 4 of the book mentioned in ref. 4). The agreement of the curves determined in these two different ways turned out to be excellent.

After these large scale matrix block NFC calculations have been performed both for non-periodic nucleotide base stacks (ref. 19) containing all the four components and with a chain length of 300 units or for four-, five- and six components polypeptides (ref. 20). In the case if the different units ABCD etc. were repeated in a periodic way $(ABCD)_n$ in all cases for all bands we have obtained only extremely narrow (δ-function like peaks) with large gaps between them. On the other hand if the sequences were chosen randomly (with the help of a Monte Carlo program) the allowed valence- and conduction band energy regions broadened to about 4 eV both with very few and narrow gaps. This gives the possibility of a hopping-type conduction. In the case of a four-component random polypeptide we have calculated explicitly the hopping frequencies and have found (ref. 20) that they are in the same order of magnitude than for good amorphous 3D conductors. This means that if non-periodic proteins are doped (especially by electron donors) they can become quite good hopping conductors.

For the case of the correlated QP band structures we want to mention also the case of trans-alternating polyacetylene. This system has (even after geometry optimization) a far too large gap if one uses a minimal basis set (8.3 eV) which decreases even if one introduces correlation using MP/2 only to 7.7 eV (ref. 12). On the other hand applying a 6-31 G** basis (double +polarization functions both on C and on H), the HF gap decreases to 4.4 eV and with MP/2 correlation to ~3 eV (ref. 12). The experimental peak is around 2 eV. For the remaining discrepancies is easy to account by the missing part of correlation which according to Suhai's estimation (ref. 12) would bring down the gap to 2.5 eV, the neglection of the relaxation of the other CO-s in the case of introducing an extra electron or hole, respectively, and finally the neglect of phonon polaron effects (rigid lattice calculations).

Finally, it should be mentioned that on the supercomputers of IBM in Poughkeepsie-Kingston (N.Y., USA) and Rome we have performed also large scale calculations to determine the effect of the water and Na^+ environments of different periodic base stacks and polypeptides both in the α-helical and ß-pleated sheet conformation. The results show generally an ~ 1 eV downward shift of both of the conduction and valence band and a band narrowing of ~ 10 per cent in these systems.

4. CONCLUDING REMARKS

From the briefly outlined formalisms and very shortly discussed illustrative examples one can see that if one starts from a good basis set HF calculation and corrects for correlation (this is possible in a somewhat tedious way also for disordered polymers), takes into account the interaction between chains in a polymeric material and the effect of environment one can obtain a good enough quality level distribution and wavefunction. With the help of them one can account for nearly any kind of physical properties of polymers in good agreement with experiment. This has been done until now for the ground state properties of $(SN)_x$ (see Chapter 2 of the several times mentioned book) for the gap of alternating transpolyacetylene (ref. 12), for the exciton spectra of polyacetylene, polydiacetylene, of a cytosine stack and for polyglycine (Chapter 8 of the book), for the vibrational spectra of periodic and non-periodic polyacetylene (Chapter 9 of the book) and for the different elastic moduli of polyethylene (Chapter 10 of the book). With the use of still more advanced supercomputers one can repeat the same kind of calculations for polymers with larger unit cells and extend the calculations to other not yet calculated properties (tansport-, magnetic- and other mechanical properties, heat conduction and resistance etc.).

On the one hand in this way one can interpret the different physical-chemical properties of polymers and on the basis of them their biological functions in the case of biopolymers. On the other hand one can start systematically to investigate different series of similar polymers to taylor them in an optimal way for required properties which could easily lead to breakthroughs in different branches of technology.

REFERENCES

1. S.G. Bednorz and K.A. Müller, Z. Phys. B64, 189 (1986).
2. M.K. Wu, J.R. Ashburn, C.J. Tornog, P.H. Hor, R.L. Meng, L. Gao, Z.J. Huang, Y.O. Wang and C.W. Chu, Phys. Rev. Lett. 58, 908 (1987).
3. C.C.J. Roothaan, Rev. Mod. Phys. 23, 69 (1951).
4. G. Del Re, J. Ladik and G. Biczó, Phys. Rev. 155, 997 (1967); J.-M. André, L. Gouverneur and G. Leroy, Int. J. Quant. Chem. 1, 427, 451 (1967); J. Ladik: Quantum Theory of Polymers as Solids, Plenum Press, New York-London, 1987, Chapt. 1 (in press).
5. A. Blumen and C. Merkel, Phys. stat. sol. 83, 425 (1977); J. Ladik, in "Excited States in Quantum Chemistry", eds. C.A. Nicolaides and D.R. Beck, D. Reidel Publ. Corp. Dordrecht-Boston-New York (1979) p. 495.
6. See the last part of ref. 4 and S. Suhai, Quantenmechanische Untersuchungen an quasi-ein-dimensionalen Festkörpern (Quantum Mechanical Investigations of Quasi-one-dimensional Solids) Habilitation Thesis, University Erlangen-Nürnberg (1983).
7. A.J. Elliott, J.A. Krumhansl and P. Leath, Rev. Mod. Phys. 46, (1974); see also F. Martino, in "Quantum Theory of Polymers", eds. J.-M. André, J. Ladik and J. Delhalle, D. Reidel Publ. Corp. Dordrecht-Boston (1978) p. 169.
8. D. Pumpernik, B. Borstnik, M. Kertész and A. Azman, Z. Naturforsch. A32, 295 (1977); M. Seel, Chem. Phys. 43, 103 (1973).
9. P. Dean, Proc. Roy. Soc. A254, 507 (1960); Rev. Mod. Phys. 44, 127 (1972).
10. R.S. Day and F. Martino, J. Phys. C: Solid State Phys. 14, 4247 (1980); R.S. Day, S. Suhai and J. Ladik, Chem. Phys. 62, 165 (1981).
11. C. Moeller and M.S. Plesset, Phys. Rev. 46, 618 (1934).
12. S. Suhai and J. Ladik, J. Phys. C: Solid State Phys. 15, 4327 (1982); S. Suhai, Phys. Rev. B27, 3506 (1983).
13. C.-M. Liegener, J. Phys. C: Solid State Phys. 18, 6011 (1983); C.-M. Liegener and J. Ladik, Chem. Phys. 106, 339 (1986); C.-M. Liegener and J. Ladik, Phys. Rev. B35, 6403 (1987).
14. J. Cizek, J. Chem. Phys. 45, 4256 (1966); J. Cizek, Adv. Quant. Chem. 3, 35 (1969); J. Cizek and J. Paldus, Int. J. Quant. Chem. 5, 359 (1971); J. Paldus and J. Cizek, Adv. Quant. Chem. 9, 105 (1975).
15. W. Förner and J. Ladik (to be published).
16. P. Otto and J. Ladik, Chem. Phys. 8, 192 (1975); J. Ladik, Int. J. Quant. Chem. S9, 563 (1975); ibid 19, 209 (1977); P. Otto, Chem. Phys. 33, 407 (1978).
17. P. Otto, Int. J. Quant. Chem. 28, 895 (1985).
18. P. Otto, J. Ladik, G. Corongiu, S. Suhai and W. Förner, J. Chem. Phys. 77, 5026 (1982).
19. A.K. Bakhshi, P. Otto, J. Ladik and M. Seel, Chem. Phys. 108, 215 (1985).
20. A.K. Bakhshi, J. Ladik, M. Seel and P. Otto, Chem. Phys. 108, 233 (1986).