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Propagators for Alternant Hydrocarbon Molecules*

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Green's functions for electron and for particle-hole propagation are calculated for even alternant hydrocarbons. With the use of three parameters, accurate correspondence is achieved between calculated and observed spectra for ethylene, benzene, naphthalene, and anthracene.

INTRODUCTION

ATTENTION is paid in this article to the possibility of a Green's-function formulation of the molecular many-electron problem. A preliminary account has been given of such an attempt[1] and the results warrant a further extended investigation into the implications of the theory.

Wide recognition has been given the Green's-function method in many-particle physics for its versatility and its appeal to physical intuition. The abundant literature on the subject concentrates on infinite systems but recently several authors have taken an interest in applications to atoms,[2] molecules,[3] and nuclei.[4] A theory for arbitrary molecules meets with certain complexities since it has to account for the electronic motion in a field which is neither homogeneous, as is assumed for metals, nor isotropic, as in atoms.

Planar unsaturated molecules lend themselves more readily than others to theoretical studies owing to the apparent validity of the sigma-pi separation.[5] There has been a considerable interest in the application of quantum-mechanical approximation methods to the eigenvalue problem arising from the so-called pi-electron Hamiltonian. A survey of such calculations has been given by Parr.[6]

The notion of elementary excitations offers a new interpretation of the pi-electron theory. It is generally conceived that various atoms in the molecule contribute mobile electrons to the conjugated system and that the states of the system can be constructed from states of the participating atoms. This holds for the molecular-orbital theory as well as for the valence-bond method. The equivalent formulation in many-particle theory says that an elementary excitation of the molecule can be considered as a superposition of atomic excitations. The resulting dynamical problem is then concerned with the interaction of the atomic excitations rather than with an assembly of real electrons.[7] Elementary excitations of quasiparticles are represented by operators which obey anticommutation relations identical to those of the electron field operators in second quantization. Quasiparticle interactions enter the theory of conjugated systems as parameters, which are determined from a correspondence between calculated and observed properties of the molecule. Ideally, it should be possible to evaluate them from first principles. The semiempirical theory originated by Hückel[8] and further extended by many authors, particularly Pariser and Parr[9] and Pople,[10] has proven to be of substantial value in the description of properties of the optical electrons of conjugated systems. One assumes in the Pariser-Parr-Pople method that the pi-electron Hamiltonian can be satisfactorily represented by the matrix elements involving only a limited set of atomic states. Even with these limitations it has become necessary to resort to approximate methods for the determination of eigenvalues and eigenstates. Pople[10] used the self-consistent Hartree-Fock method, while Pariser and Parr[9] preferred the method of limited superposition of configurations. The former approach neglects correlation phenomena and the latter rapidly becomes rather unsystematic as there are no rules for the choice of configurations.

Coulson and Longuet-Higgins[11] demonstrated how the properties of the conjugated system can be calculated from the resolvent of the effective single-particle

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[1] J. Linderberg and Y. Öhrn, Proc. Roy. Soc. (London) **A285**, 445 (1965).

[2] W. Brandt and S. Lundqvist, Phys. Rev. **132**, 2135 (1963). V. Aliamovskij and D. Kirzhuits, Lietuvos Fizikos Rinkinys **III**, 92 (1963).

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[4] G. E. Brown, *Unified Theory of Nuclear Models* (North-Holland Publishing Company, Amsterdam, 1964). D. J. Thouless, Rept. Progr. Phys. **27**, 53 (1964). A. Migdal, Nucl. Phys. **57**, 29 (1964).

[5] P. G. Lykos and R. G. Parr, J. Chem. Phys. **24**, 1166 (1956).

[6] R. G. Parr, *Quantum Theory of Molecular Electronic Structure* (W. A. Benjamin, Inc., New York, 1963).

[7] L. D. Landau, Zh. Eksperim. i Teor. Fiz. **30**, 1058 (1956); **32**, 59 (1957) [English transls.: Soviet Phys.—JETP **3**, 920 (1957); **5**, 101 (1957)].

[8] E. Hückel, Z. Physik **70**, 204 (1931).

[9] R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466 (1953).

[10] J. A. Pople, Trans. Faraday Soc. **49**, 1375 (1953).

[11] C. A. Coulson and H. C. Longuet-Higgins, Proc. Roy. Soc. (London) **A191**, 39 (1947).

Hamiltonian. Their results were obtained for a system of noninteracting particles, but they remain valid for an interacting system if the resolvent is replaced by the single-particle Green's function. Pople's method can relatively easily be extended to include a certain amount of correlation effects by the application of an idea due to Hubbard,[12] as is elaborated in Ref. 1. The strength and unity of the Green's-function approach allows the direct evaluation of characteristic properties without explicit reference to eigenstates. In particular one obtains the energy levels of the system as referred to the ground-state energy without specifying the latter.

We describe in the following section the principal assumptions used in the derivation of the fundamental equation of the theory and present arguments which serve to give a physical interpretation of the processes considered. The equation is then solved for the case of even alternant hydrocarbons. The results of these calculations are then used, in the third section, to derive an equation for a two-particle Green's function from which we determine the absorption frequencies for so-called particle-hole excitations. Results are reported for ethylene, benzene, naphthalene, and anthracene in Sec. 4.

A DYSON EQUATION

The operation of adding an electron to a molecule at the point $\mathbf{r}$ and time t with spin component η will be represented by the Heisenberg operator $\psi_\eta^\dagger(\mathbf{r},t)=\psi^\dagger(x)$, while the adjoint operator effectuates the removal of a particle from the system. The variable x serves as a combined coordinate for space, spin, and time. Eigenstates of the molecule are characterized by their energy and the number of particles in the state. Green's functions or propagators[13] are defined as

$$\begin{aligned}G(x,x')=i\theta(t'-t)\langle E_0,N|\psi^\dagger(x')\psi(x)|E_0,N\rangle\\ -i\theta(t-t')\langle E_0,N|\psi(x)\psi^\dagger(x')|E_0,N\rangle,\end{aligned}\qquad(1)$$

$$\begin{aligned}\theta(t)&=0\quad t<0\\ &=1\quad t>0,\end{aligned}\qquad(2)$$

where E_0 is the ground-state energy for the N-electron system. One interprets $iG(x,x')$ as the probability amplitude that the disturbance created by introducing an electron at x' will develop into the state where an electron can be removed at x ($t>t'$) leaving the system in the ground state. For $t<t'$, the interpretation is reversed with regard to creation and annihilation. It is clear that $G(x,x')$ depends upon time through the interval t-t', and we will mostly consider its Fourier components

$$G^\eta(\mathbf{r},\mathbf{r}';E)=\int_{-\infty}^{\infty}G^\eta(\mathbf{r}t;\mathbf{r}'0)e^{iEt/\hbar}dt,\qquad(3)$$

where it is implicitly understood that G is diagonal in its spin variables.

A molecular theory will be developed from the assumption that for the elementary excitations it is satisfactory to expand the operator $\psi(x)$ into a limited set of atomic orbitals which should be orthonormalized in a suitable fashion.[14] Only one orbital per atom is introduced for the study of conjugated systems. The expansion coefficients will be called $a_{s\eta}(t)$ and represent atomic excitations. The quantities $G_{rs}^\eta(t-t')$ are the expressions (1) applied to operators $a_{r\eta}(t)$ and $a_{s\eta}^\dagger(t')$. It has been shown by Hubbard[12] that when correlation between operators referring to different centers is neglected while atomic correlations are included one obtains an equation for the calculation of $G_{rs}^\eta(E)$ in the form of a Dyson equation

$$G_{rs}^\eta(E)=D_{rs}^\eta(E)+\textstyle\sum_{u,v}D_{ru}^\eta(E)\beta_{uv}G_{vs}^\eta(E).\qquad(4)$$

The propagator $D_{rs}^\eta(E)$ is diagonal in atomic labels and represents G in the case when there are no interactions between atomic excitations. Accordingly, β_{uv} accounts for the scattering of excitations from site v to site u.

The particular case of even alternant hydrocarbons admits a simple solution of (4), since it can be assumed that all atoms are similar because of the Coulson-Rushbrooke theorem,[15] and that the two spin directions are equivalent. Then we have

$$D_{rs}^\eta(E)=\delta_{rs}D(E).\qquad(5)$$

We choose the matrix $\{\beta_{uv}\}$ according to the common practice in Hückel theory and it is then possible to express its elements in terms of the eigenvalues and eigenvectors of the topological matrix[16]

$$\beta_{uv}=\beta\textstyle\sum_j c_{uj}k_jc_{vj}^*.\qquad(6)$$

Introducing the function

$$G(k,E)=\frac{D(E)}{1-\beta kD(E)},\qquad(7)$$

we find the solution of (4) as

$$G_{rs}(E)=\textstyle\sum_j c_{rj}G(k_j,E)c_{sj}^*.\qquad(8)$$

In order to discuss this solution further, we need to consider the analytical properties of $D(E)$.

The very simplest approximation to $D(E)$ is obtained when one assumes that it can be considered as independent of the interatomic interactions. Then it is the asymptotic form of $G_{rr}(E)$ in the limit of separated

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[12] J. Hubbard, Proc. Roy. Soc. (London) **A276**, 238 (1963).

[13] We follow the conventions given by A. A. Abrikosov, L. P. Gorkov, and I. E. Dzyaloshinski, *Methods of Quantum Field Theory in Statistical Physics* (Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1963).

[14] P. O. Löwdin, J. Chem. Phys. **18**, 365 (1950).

[15] C. A. Coulson and G. S. Rushbrooke, Proc. Cambridge Phil. Soc. **36**, 193 (1940).

[16] K. Ruedenberg, J. Chem. Phys. **29**, 1232 (1958).

atoms. The spectral representation[13] of $G_{rr}(E)$ is

$$G_{rr}(E)=\int_0^\infty\left[\frac{A(r,\omega)}{E-\omega-\mu+i\delta}+\frac{B(r,\omega)}{E+\omega-\mu-i\delta}\right]d\omega. \tag{9}$$

$A(r,\omega)$ and $B(r,\omega)$ are spectral density functions. They are positive definite and obey the sum rules[17]

$$\begin{aligned}\int_0^\infty A(r,\omega)d\omega&=\langle E_0,N|a_r a_r^\dagger|E_0,N\rangle=1-\langle n_r\rangle,\\ \int_0^\infty B(r,\omega)d\omega&=\langle E_0,N|a_r^\dagger a_r|E_0,N\rangle=\langle n_r\rangle.\end{aligned} \tag{10}$$

The average value $\langle n_r\rangle$ is the probability of finding an electron on site r with a prescribed spin component. In the case we are studying $\langle n_r\rangle=\frac{1}{2}$ since all atoms are equivalent as are the two spin directions. A description in terms of elementary excitations is now possible since an elementary excitation is represented by a pole of the Green's function.[13] Only two such excitations are possible for separated atoms, viz., the formation of positive or negative ions. These processes correspond to poles of $G_{rr}(E)$ at

$$E=E_0(N-1)-E_0(N) \quad\text{and}\quad E=E_0(N)-E_0(N+1),$$

respectively, where $E_0(N)$ is the ground-state energy of the N-electron system. We choose

$$\mu=\tfrac{1}{2}[E_0(N-1)-E_0(N+1)]$$

and

$$\gamma=E_0(N-1)+E_0(N+1)-2E_0(N)$$

from which we arrive at the simple form

$$D(E)=\frac{\frac{1}{2}}{E-\mu-\frac{1}{2}\gamma+i\delta}+\frac{\frac{1}{2}}{E-\mu+\frac{1}{2}\gamma-i\delta}. \tag{11}$$

The form of $G(k,E)$ is then simply found to be

$$G(k,E)=\frac{A(k)}{E-\mu-\epsilon(k)+i\delta}+\frac{A(-k)}{E-\mu+\epsilon(-k)-i\delta} \tag{12}$$

with

$$A(k)=\tfrac{1}{2}[1+\beta k(\gamma^2+\beta^2k^2)^{-1/2}] \tag{13}$$

and

$$\epsilon(k)=\tfrac{1}{2}[\beta k+(\gamma^2+\beta^2k^2)^{1/2}]. \tag{14}$$

It has been demonstrated[1] that this solution is consistent with the Coulson-Rushbrooke theorem.[15]

A BETHE-SALPETER EQUATION

When two elementary excitations are simultaneously agitated in a system, one can derive the stationary states from a study of an appropriate Bethe-Salpeter equation.[17a] The description of excited states of the N-electron system requires an examination of the propagation of particle-hole pairs. The operator which creates such a pair on atom r without change of spin component is

$$\rho_{r\eta}(t)=a_{r\eta}^\dagger(t)a_{r\eta}(t)-\langle a_{r\eta}^\dagger a_{r\eta}\rangle. \tag{15}$$

The last term accounts for the elimination of the ground-state component in the new state. We define the Green's function

$$\begin{aligned}Q_{rs}^{\eta\eta'}(t-t')=&-i\theta(t-t')\langle E_0,N|\rho_{r\eta}(t)\rho_{s\eta'}(t')|E_0,N\rangle\\ &-i\theta(t'-t)\langle E_0,N|\rho_{s\eta'}(t')\rho_{r\eta}(t)|E_0,N\rangle,\end{aligned} \tag{16}$$

which describes the motion of the pair from atom s to atom r in the time interval $t-t'$, and argue that, when no interaction takes place between the particle and the hole, it is equal to the free propagator

$$P_{rs}^{\eta}(t-t')=-iG_{rs}^{\eta}(t-t')G_{sr}^{\eta}(t'-t). \tag{17}$$

The Fourier components of Q and P are defined as in (3) and, in particular,

$$P_{rs}^{\eta}(E)=\frac{1}{2\pi i}\int_{-\infty}^{\infty}dE'G_{rs}^{\eta}(E')G_{sr}^{\eta}(E'-E). \tag{18}$$

It is possible to derive an equation for Q in terms of the known function P if we disregard scattering processes which will separate the particle and the hole to different atoms. This approximation is similar to the zero differential overlap approximation.[18] The propagation of a particle-hole pair will be strongly influenced by repeated interactions between the particle and the hole, and, as a first approximation, we will consider only instantaneous interactions on one center. Consequently, we obtain the desired Bethe-Salpeter equation as

$$Q_{rs}^{\eta\eta'}(E)=\delta_{\eta\eta'}P_{rs}^{\eta}(E)+\textstyle\sum_u P_{ru}^{\eta}(E)V_uQ_{us}^{-\eta\eta'}(E). \tag{19}$$

The element V_u connects propagators of different spin only because of the Pauli principle and corresponds to the Coulomb repulsion between similar charges on the atom u, as discussed by Brandt and Lundqvist.[2]

Excitation frequencies for particle-hole pairs are given by the poles of Q and they can be calculated from the homogeneous equation system.[19]

$$\chi_r^{\eta}=\textstyle\sum_u P_{ru}^{\eta}(E)V_u\chi_u^{-\eta}. \tag{20}$$

We can separate out singlet and triplet excitations from (20) when the ground state is a singlet state and $P_{ru}^{\eta}(E)$ is independent of the spin component.[19] Thus, we have

$$\chi_r^{\pm}=\pm\textstyle\sum_u P_{ru}(E)V_u\chi_u^{\pm} \tag{21}$$

for singlets (+) and triplets (−), respectively.

A calculation of $P_{rs}(E)$ for aromatic hydrocarbons

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[17] P. Nozières, *Theory of interacting Fermi systems* (W. A. Benjamin, Inc., New York, 1964), p. 348.

[17a] See Ref. 17, p. 240.

[18] R. G. Parr, J. Chem. Phys. **20**, 1499 (1952).

[19] V. M. Galitskii and A. B. Migdal, Zh. Eksperim. i Teor. Fiz. **34**, 139 (1958) [English transl.: Soviet Phys.—JETP **7**, 97 (1958)].

gives

$$P_{rs}(E)=\sum_{\mu\nu} f_{rs}{}^{\mu\nu}/[E^2-\omega_{\mu\nu}{}^2]. \tag{22}$$

The notations are

$$f_{rs}{}^{\mu\nu}=2c_{r\mu}c_{r\nu}c_{s\mu}c_{s\nu}A(k_\mu)A(-k_\nu)\omega_{\mu\nu} \tag{23}$$

and

$$\omega_{\mu\nu}=\epsilon(k_\mu)+\epsilon(-k_\nu). \tag{24}$$

It is possible to interpret $\omega_{\mu\nu}$ as the unperturbed energy for creation of a particle in the molecular orbital μ and a hole in the orbital ν. The condition for the existence of a solution of (21) is

$$\|(1/V)\delta_{rs}\mp P_{rs}(E)\|=0. \tag{25}$$

Equation (25) is satisfied when an eigenvalue of the matrix $\{P_{rs}(E)\}$ equals $\pm V^{-1}$.

RESULTS

Three parameters enter the calculation of spectra for the even alternant hydrocarbons, i.e., γ, β, and V in the notation of this paper. The quantity γ is the difference between the ionization potential and electron affinity for a carbon atom pi-electron when no interactions are present between atoms. Mulliken[20] has estimated this to 10.53 eV, and we will use that value in the calculations. It is advantageous to employ γ as the unit of energy and we have chosen $\beta=0.46\,\gamma=4.84$ eV as the most appropriate value for the interatomic parameter.[21]

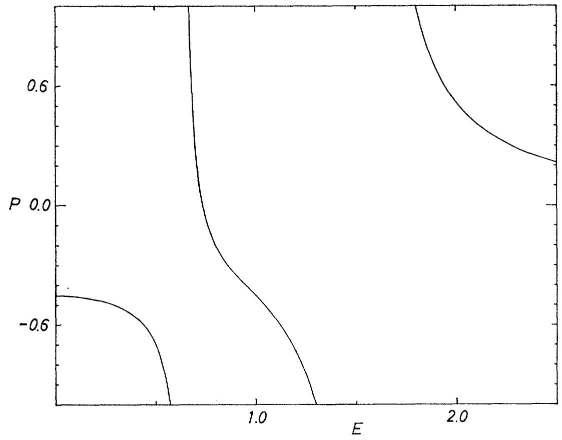

FIG. 1. Eigenvalue of $\{P_{rs}(E)\}$ in units of γ^{-1} versus energy E in units of γ for ethylene, B_{1u} symmetry.

The calculation of the eigenvalues of $\{P_{rs}(E)\}$ as functions of E/γ was performed by diagonalization of the matrix on an electronic computer. Molecular symmetry properties were used to reduce the dimension of the eigenvalue problem. Plots of the functions are given for ethylene (Fig. 1), benzene (Fig. 2), and naphthalene (Figs. 3 and 4). Solutions to Eq. (25) are found from the intersections of the curves with the lines $\pm\gamma/V$. It was argued in the preceding section that V should be the electronic repulsion integral $(2p\pi 2p\pi|2p\pi 2p\pi)$ for carbon. The theoretical value is in the range 16–18 eV, depending upon the choice of orbitals.

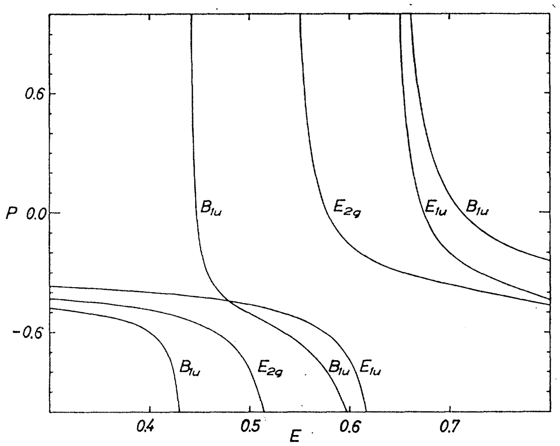

FIG. 2. Eigenvalues of $\{P_{rs}(E)\}$ in units of γ^{-1} versus energy E in units of γ for benzene.

TABLE I. Energy levels of ethylene.[a]

State	Observed[b]	Calculated with $V=17.55$	16.85	16.20
^1A_g	0	0	0	0
$^3B_{1u}$	4.6	4.63	4.84	5.02
$^1B_{1u}$	7.66	7.16	7.16	7.15

[a] All energies in eV.
[b] Reference 24.

Our results are presented in Tables I–IV. In order to illustrate the variation of the energy levels with V we have listed calculations for three representative values of the ratio γ/V, 0.6, 0.625, and 0.65. The calculations compare favorably with the observed spectra, which

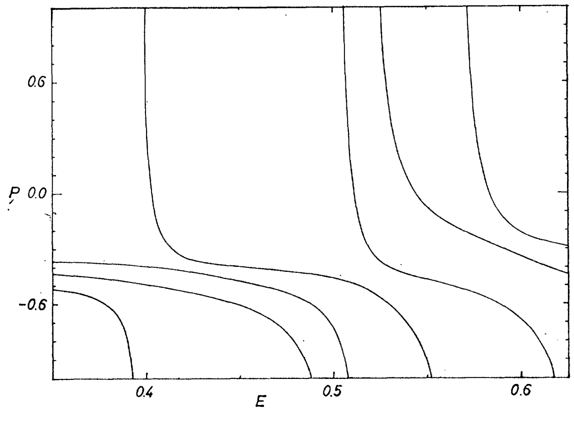

FIG. 3. Eigenvalues of $\{P_{rs}(E)\}$ in units of γ^{-1} versus energy E in units of γ for naphthalene, B_{2u} symmetry.

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[20] R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934).
[21] R. McWeeny and T. Peacock, Proc. Phys. Soc. (London) **A70**, 41 (1957).

TABLE II. Energy levels of benzene.[a]

Observed[b]		Calculated	
Symmetry	Energy	Symmetry	Energy ($V=17.55$)
$^1A_{1g}$	0	$^1A_{1g}$	0
$^1B_{2u}$	4.89	$^1B_{1u}$	4.66
$^1B_{1u}$	6.14	$^1E_{2g}$	5.84
$^1E_{1u}$	6.75	$^1E_{1u}$	6.90
$^3B_{1u}$	3.66	$^3B_{1u}$	4.22
$^3E_{1u}$	4.69	$^3E_{2g}$	4.91
$^3B_{2u}$	5.76	$^3B_{1u}$	5.62
		$^3E_{1u}$	6.07

[a] All energies in eV.
[b] Reference 23.

TABLE III. Energy levels of naphthalene.[a]

Observed[b]		Calculated			
			Energy		
Symmetry	Energy	Symmetry	$V=17.55$	16.85	16.20
^1A_g	0	^1A_g	0	0	0
$^1B_{2u}$	4.34	$^1B_{2u}$	4.21	4.21	4.21
	7.41		5.34	5.34	5.34
			5.56	5.56	5.56
			5.94	5.94	5.93
$^1B_{3u}$	3.97	$^1B_{3u}$	5.69	5.69	5.68
	5.63		6.16	6.16	6.16
		^1A_g	5.15	5.15	5.15
			6.44	6.44	6.44
			6.78	6.78	6.78
		$^1B_{1g}$	4.77	4.77	4.77
			6.16	6.16	6.16
$^3B_{2u}$	2.64	$^3B_{2u}$	3.98	4.01	4.04
			4.72	4.79	4.84
			5.14	5.17	5.20
			5.57	5.60	5.63
$^3B_{1g}$	5.64	$^3B_{1g}$	4.40	4.45	4.50
	5.82		5.37	5.41	5.47
	5.98		6.00	6.09	6.15
		^3A_g	4.62	4.66	4.72
			5.80	5.85	5.90
			6.20	6.22	6.24
		$^3B_{3u}$	5.08	5.14	5.19
			5.88	5.89	5.90

[a] All energies in eV.
[b] Reference 22.

TABLE IV. Energy levels of anthracene.[a]

Observed[b]		Calculated	
Symmetry	Energy	Symmetry	Energy ($V=17.55$)
^1A_g	0	^1A_g	0
$^1B_{2u}$	3.40	$^1B_{2u}$	4.01
	4.96		4.64
			4.90
	5.60		5.70
			5.78
			5.81
	6.69		6.81
			6.91
$^1B_{3u}$	5.24	$^1B_{3u}$	5.20
			5.44
$^3B_{2u}$	1.85	$^3B_{2u}$	3.90

[a] All energies in eV.
[b] Reference 22.

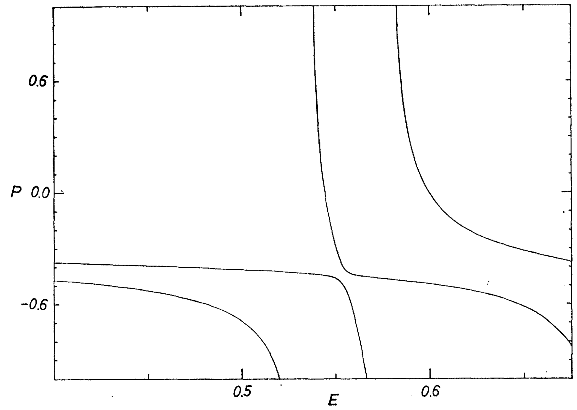

FIG. 4. Eigenvalues of $\{P_{rs}(E)\}$ in units of γ^{-1} versus energy E in units of γ for naphthalene, B_{3u} symmetry.

we have taken from the critical analysis of available data by Skancke[22] for naphthalene and anthracene and from Kearns[23] and Mulliken[24] for benzene and ethylene, respectively.

DISCUSSION

An alternative is offered in this paper to the methods in use for theoretical descriptions of the electronic spectra of conjugated systems. Applications to some aromatic hydrocarbons have shown that the theory is capable of giving results, which correspond accurately to observed excitation energies, and which can be calculated with only a small computational effort. The number of parameters is small and they can be transferred from earlier theories.

There is room for further improvement of the procedures developed here. Most certainly, one must not think that an atom in a molecule has the same resonant frequencies as a free atom. Hubbard[25] has discussed the implications of the interatomic scattering processes on the form of the propagator $D(E)$. His result takes the form that the atomic resonances are broadened and that accordingly the form (11) is an inadequate representation of $D(E)$ for strong interactions between atomic excitations. Modifications in $D(E)$ will influence the result of the determination of particle-hole excitation frequencies. The latter will also change when we allow for separation of particles and holes on to different atoms. Particle-hole pairs as described here are known in solid-state theory as Frenkel excitons,[26] and, allowing for long-range interactions between particles and holes, leads to a study of Wannier excitons.[26]

The data presented on spectra in the preceding section show that a multitude of possible levels lie within

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[22] P. N. Skancke, Acta Chem. Scand. **18**, 1671 (1964).
[23] D. R. Kearns, J. Chem. Phys. **36**, 1608 (1962).
[24] R. S. Mulliken, J. Chem. Phys. **33**, 1596 (1960).
[25] J. Hubbard, Proc. Roy. Soc. (London) **A281**, 401 (1964).
[26] R. S. Knox, *Theory of Excitons* (Academic Press Inc., New York, 1963).

TABLE V. Principle absorption energy for some hydrocarbons.[a]

Species	Benzene	Naphthalene	Anthracene
Calculated	6.90	5.69	5.20
Observed	6.75	5.63	5.24

[a] All energies in eV.

the region subjected to experimental studies. We have not calculated oscillator strengths for the corresponding transitions, but we expect that, in general, they should be small due to the strong mixing of configurations in the theory.[1] The principle absorption peak in the spectrum is given very accurately by the present theory as is shown in Table V.

Pariser[27] found it possible to give a further classification of the states of even alternant hydrocarbons. His results are dependent upon the dispersion law for quasiparticle energies. The present theory does not give rise to such a classification.

The research reported is an attempt to show that Green's function methods could be used with advantage in molecular theory, and we hope to elaborate the approach further.

ACKNOWLEDGMENTS

Professor Per-Olov Löwdin has supported and guided this investigation. We are indebted to Professor Stig Lundqvist for valuable advice and stimulating interest and to K. V. Mäkilä for able assistance with the computations. Free time has been granted by Umeå University on its IBM 1620 computer.

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[27] R. Pariser, J. Chem. Phys. 24, 250 (1956).

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Dissociation of Molecular Hydrogen Ions Enhanced by Ion-Source Operation*

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The cross section for the dissociation reaction $H_3^+ + H_2 \rightarrow H_2^+ + H + H_2$ increased by a factor of about 4 when the rf ion-source magnet field was raised. This increase is attributed to H_3^+ ions in high vibrational states. The energy dependence of the cross section was measured. Excited ions increased from 6 Å^2 at 5 keV to 10 Å^2 at 50 keV, whereas the normal ions increased from 1.5 to 2.5 Å^2 over the same energy range. The companion reaction cross section, for H_3^+ producing H^+, was 0.5 Å^2 at 5 keV increasing to 1.6 Å at 35 keV. Cross sections were about 0.25 Å^2 higher for excited ions than for normal ions. The cross section for dissociation of H_2^+ to H^+ was about 1.6Å^2 from 5 to 45 keV. H_5^+ was detected; its dissociation to H^+ with one-fifth the energy gave a cross section of 3.2 Å^2 at 20 keV, independent of source condition. Excited H_3^+ may be a useful ion for transverse injection into a magnetically confined plasma.

INTRODUCTION

THERE are cases where investigators may obtain differing cross sections for dissociation or charge transfer because their molecular ions have varied distributions of vibrational states. Such a change in the dissociation of H_3^+ and H_2^+ was detected by McClure[1] when he changed his Penning ion-source conditions. The dissociation of H_2^+ was also studied by McGowan and Kerwin.[2] The present work investigates changes in dissociation when an rf-excited ion source is employed. Such data are required in interpreting experiments in which fast neutral products are detected; from these experiments electron-capture cross sections may be obtained.[3] In addition, the present work studies in more detail the effect of source parameters on dissociation. Fast charged products from both H_3^+ and H_2^+ with energies from 5 to 50 keV have been measured as currents after magnetic analysis.

In the ion source, H_2^+ is formed by electron ionization. McGowan and Kerwin[2] have shown the increase in subsequent collisional dissociation that results from increasing the source electron energy. With H_2^+ the Franck-Condon principle puts an upper bound on the vibrational level that can be reached. With H_3^+, however, the excess energy of formation can excite the higher vibrational states. Three of the possible reactions forming H_3^+ follow. The heats of formation were calculated using the results of Hirschfelder.[4]

$$H_2^+ + H_2 \rightarrow H_3^+ + H + 0.9\text{ eV},$$

$$H^+ + H_2 \rightarrow H_3^+ + 3.5\text{ eV},$$

$$H_2^+ + H \rightarrow H_3^+ + 5.4\text{ eV}.$$

The first reaction has been studied by Stevenson and

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[1] G. W. McClure, Phys. Rev. **130**, 1852 (1963).

[2] J. M. McGowan and L. Kerwin, Can. J. Phys. 42, 972 (1964).

[3] E. S. Chambers, Lawrence Radiation Laboratory, Livermore, Report No. UCRL-6987 Rev. 1 (unpublished).

[4] J. D. Hirschfelder, J. Chem. Phys. 6, 795 (1938).