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Calculations of the Electronic Structures of Cage Molecules Using Free-Electron Orbitals as a Basis

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A non-empirical molecular orbital method, particularly suitable for calculations on cage-like molecules, is described. The method uses as basis functions the set of free-electron functions which are the solutions of Schrödinger's equation for an electron confined between two concentric, spherical potential energy barriers. Application of the theory to the SCF calculation of the energies of the delocalized electrons in benzene and tetrasulphur tetranitride shows that the model is capable of interpreting the properties of such systems. However, it does highlight a difficulty in the calculation of excited state energies with one-centre models which appears to be largely unrecognized.

Extension of the method to a consideration of all the valence electrons, using P_4 as an example, reveals problems the origin of which is an inadequate treatment of the core electrons. It is suggested that these problems may best be dealt with by use of a suitable pseudo potential.

Key words: Cage molecules, electronic structure of ~

1. Theory

The free-electron approach to the description of electronic structure has been applied to a variety of molecules [1–7]. Such an approach is essentially a topological one, inasmuch as the shape of the potential box in which the free electrons move is directly related to the shape of the molecule itself.

In spite of the drastic nature of the assumptions in the free electron model, the approach embodies a number of advantages, among which are:

a) Conceptual simplicity – the potential in which the electrons move, and the free-electron orbitals themselves are generally readily visualized [8].
b) Computational simplicity – a much smaller amount of computer time is needed than for more rigorous calculations [9–14] and useful results may often be obtained using nothing more sophisticated than pen and paper [15, 16] as in the remarkable results of Chapman and Waddington [16].

In view of these advantages, free-electron models may perhaps have been under-utilized since Hartree–Fock caclulations on small molecules of chemical interest became feasible. In this paper we consider the refinement of a free-electron model, developed by Hunter [1, 2] for F-centres in alkali halides, and its application to cage-like molecules for which the model is topologically suitable. Hoffmann and Gouterman [17] have also described a similar model but do not appear to have developed it further.

1.1. *The Free-Electron Model*

In Hunter's model [1, 2] the most loosely bound electrons in the molecular system are confined within a region of zero potential energy, bounded by two concentric spherical potential barriers of infinite height. In a cage-like molecule all, or nearly all, the atoms of the molecule will be within this region and they, being positively charged since they have lost electrons to the free-electron system, create the potential energy well. This is exactly analogous to the well-known free-electron theory of conjugated hydrocarbons.

Placing the origin of coordinates at the centre of the two concentric spherical potential barriers, the Schrödinger equation may be solved by assuming a solution of the form:

$$\psi = R(r) \cdot \Theta(\theta) \cdot \Phi(\phi). \tag{1}$$

The separation of the variables proceeds in the usual way [18] and since the potential has spherical symmetry about the origin, the angular solutions are identical [19] with the spherical harmonics obtained in the solutions of the Schrödinger equation for the hydrogen atom.

$$\psi = R(r) Y_{lm}(\theta, \phi). \tag{2}$$

The radial part of the wave function, $R(r)$, must satisfy the equation:

$$\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + 2r^2E = l(l+1) \tag{3}$$

which can readily be converted into Bessel's equation of half-integral order, for which the solutions are [20]:

$$R(r) = r^{-1/2}\,[AJ_{l+1/2}(kr) + BJ_{-l-1/2}(kr)] \tag{4}$$

In Eq. (4) $J_{l+1/2}$ and $J_{-l-1/2}$ are Bessel functions of half-integral order and A and B are constants.

Thus, the complete free-electron orbitals are given by Eq. (5) in which n, l, and m are quantum numbers and N' is a normalizing factor.

$$\psi_{n,l,m} = N'r^{-1/2}\,[AJ_{l+1/2}(kr) + BJ_{-l-1/2}(kr)]\,Y_{lm}(\theta, \phi), \tag{5}$$

k is related to the one-electron orbital energy, E (in atomic units), by Eq. (6).

$$k = (2E)^{1/2}. \tag{6}$$

1.2. *The Orbital Energies*

The requirement that the radial function (4) goes to zero at r_α and r_β, the radii of the inner and outer potential barriers respectively, gives the condition:

$$J_{l+1/2}(kr_\alpha)J_{-l-1/2}(kr_\beta) - J_{l+1/2}(kr_\beta)J_{-l-1/2}(kr_\alpha) = 0 \tag{7}$$

which determines k, and hence E, the orbital energy, as a function of the shell radii and the quantum number l. The dependence of the orbital energy upon the values of r_α and r_β is shown in Fig. 1. The energy, E, is plotted against $2(r_\beta - r_\alpha)/(r_\beta + r_\alpha) = \Delta$ for an average radius, $r_0 = (r_\beta + r_\alpha)/2$, of 1.74 Å. The notation for the orbitals is of the form nl where n gives the number of radial nodes in the wave function, plus 1, and the l value is denoted by s, p, d etc.: as in the hydrogen atom.

1.3. *The Normalization of the Wave Functions*

It is convenient to make the substitution $Q = B/A$ in Eq. (4) which allows us to write the radial wave function in the marginally abbreviated form:

$$R(r) = Nr^{1/2}\ [J_{l+1/2}(kr) + QJ_{-l-1/2}(kr)]. \tag{8}$$

Once k has been found Q may be determined from either of the conditions, $R(r_\alpha) = R(r_\beta) = 0$. When the inner radius is zero Q becomes zero.

We normalize $R(r)$ according to Eq. (9),

$$\int_{r_\alpha}^{r_\beta} \{R(r)\}^2\ r^2\,dr = 1, \tag{9}$$

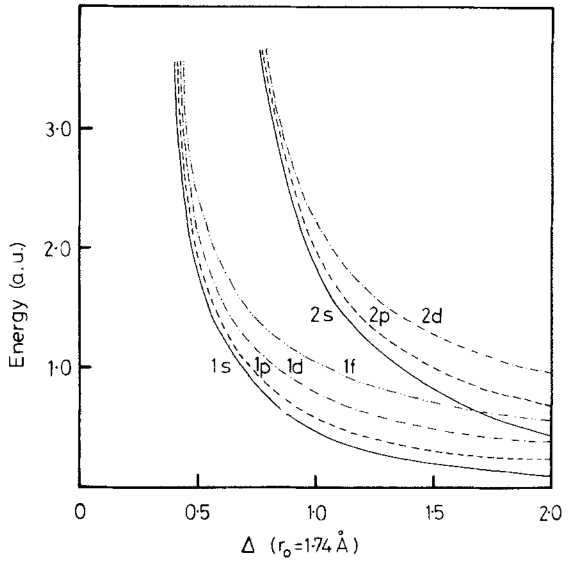

Fig. 1. Orbital energies (a.u.) as a function of $\Delta\ \{= 2(r_\beta - r_\alpha)/(r_\beta + r_\alpha)\}$, $r_0 = (r_\beta + r_\alpha)/2 = 1.74$ Å

simplifying the integral by means of the properties of Bessel and cylinder functions [20] to give:

$$N^{-2} = QJ_{-l-3/2}\{J_{l-1/2} - QJ_{-l+1/2}\} + 2QJ_{l+3/2}J_{-l+1/2}. \tag{10}$$

Our purpose is to use the free-electron wave functions described above as a basis for a self-consistent field calculation of the electronic structures of cage-like molecules, restricting the calculation, however, to the most loosely bound electrons. That is we consider the remaining electrons, together with the nuclei, to form a set of point charges which provide the potential field in which the labile electrons move. This is clearly a rather drastic approximation. However, it should be to some extent compensated by the fact that with the limited basis sets at our disposal we would not expect to produce high electron densities in the immediate neighbourhood of the nuclei. The empirical choice of the Hamiltonian and the restriction of the basis set represent the only approximations in the model.

In order to proceed with the calculations two more quantities must be evaluated; the electron-atomic core attraction and the interelectronic repulsion.

1.4. *The Electron-Core Attraction*

The atomic cores are assumed to be point charges having spherical polar coordinates r_n, θ_n, ϕ_n and the matrix elements of the electron-core attraction are given by Eq. (11).

$$\langle \psi_\mu(i) \left| \frac{eq_n}{r_{in}} \right| \psi_\nu(i) \rangle = -eq_n \cos(m_\mu - m_\nu)\phi_n$$

$$\sum_{k=0}^{\infty} \left(\frac{2}{2k+1} \right)^{1/2} \Theta_k^{m_\mu - m_\nu} (\theta_n) C^k(l_\mu m_\mu \cdot l_\nu m_\nu)$$

$$\left\{ \int_{r_\alpha}^{r_n} \frac{r_i^{k+2}}{r_n^{k+1}} R_\mu(r) R_\nu(r)\, dr_i + \int_{r_n}^{r_\beta} \frac{r_n^k}{r_i^{k-1}} R_\mu(r) R_\nu(r)\, dr_i \right\}. \tag{11}$$

Equation (11) is simply a slightly modified form of the expression for interelectronic repulsion in atoms [21] and all the symbols used have the meaning which they have in that context. It is very tedious to evaluate any but the simplest of the radial integrals of Eq. (11) in closed form, and we have found it preferable to calculate them numerically using Gaussian quadrature [22].

1.5. *The Electron-Electron Repulsion*

The matrix elements of the electron-electron repulsion operator can be readily expressed in a form effectively identical to that for the corresponding matrix elements in atoms [21], Eq. (12).

$$\langle \psi_\mu(i)\,\psi_\nu(j)\left|\frac{e^2}{r_{ij}}\right|\psi_\rho(i)\,\psi_\sigma(j)\rangle = e^2$$

$$\sum_k C^k(l_\mu m_\mu, l_\rho m_\rho)\cdot C^k(l_\sigma m_\sigma, l_\nu m_\nu)$$

$$\left\{\int_{r_\alpha}^{r_\beta} R_\mu(r_i)R_\rho(r_i)r_i^{1-k}dr_i \int_{r_\alpha}^{r_i} R_\nu(r_j)R_\sigma(r_j)r_j^{k+2}dr_j\right.$$

$$\left.+\int_{r_\alpha}^{r_\beta} R_\mu(r_i)R_\rho(r_i)r_i^{k+2}dr_i \int_{r_i}^{r_\beta} R_\nu(r_j)R_\sigma(r_j)r_j^{1-k}dr_j\right\}. \qquad (12)$$

No general method of evaluating the radial integrals above has been found, but they can be readily determined using linked Gaussian quadrature [22–24]; Appendix A.

With the aid of the integrals calculated above, an iterative self-consistent field calculation can be carried out and the radii r_α and r_β varied to find the lowest total energy of the system.

2. Applications

The area of application of the theory outlined above appears, first and foremost, to be the electronic properties of those cage-like molecules which are believed to contain a significant number of delocalized electrons. By delocalized electrons we shall mean those which have substantial densities on more than two atoms, and for which the eigenfunctions of the Fock operator cannot be transformed to any localized form; e.g. the π-electron orbitals of benzene. Metal clusters, the polyhedral frameworks of boranes and carboranes and cages of elements of groups V and VI such as S_4N_4 and P_4S_3, are examples which immediately come to mind. Cage molecules in which the bonding electrons are highly localized, cubane for instance, would not be suitable cases for calculation by this model.

The method seems particularly well suited to the description of the electronic spectra, and related properties, of molecular cages since such properties are known to be largely determined (in the readily accessible regions) by the delocalized electrons. Further, the successful interpretation of electronic spectra depends critically upon a correct ordering of energy levels which, in turn, requires either extensive parametrization or accurate evaluation of electron repulsion integrals. The model described here is capable of providing all the required electron interaction integrals without neglect, approximation or parametrization. We illustrate the method with trial calculations on tetrasulphur tetranitride (Fig. 2) and benzene, although the latter is perhaps not well suited to our method since, being planar, it creates some redundancy in the basis set.

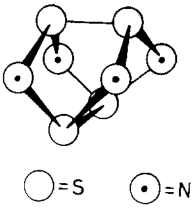

Fig. 2. The structure of tetrasulphur tetranitride, S_4N_4

2.1. *Tetrasulphur Tetranitride* S_4N_4

There is no general agreement as to the number of electrons involved in the delocalized system of this molecule. Chapman and Waddington [16], Gleiter [25] and Mingos [26] have proposed eight while Banister [15] has suggested twelve. We have used eight electrons for the following reasons. Firstly, a satisfactory orbital scheme for the remaining valence electrons can be set up involving two-electron S-N bonds, lone pairs and an S-S bond between adjacent sulphur atoms [27]. The existence of the latter bond is fairly well established, and Turner and Mortimer [28] even suggest that it is a pure σ interaction. Secondly, the principal alternative, 12 electrons, implies using an effective nuclear charge of two units on sulphur. This would be expected to produce a rather heavily localized electron density in the region of the sulphur atoms which basis sets such as the one used here cannot describe accurately without using a very large number of basis functions. We therefore consider eight delocalized electrons but allow charge polarization of the sulphur and nitrogen cores. Thus, if Q_N and Q_S are the positive charges on nitrogen and sulphur respectively, then we require that $Q_N + Q_S = 2.0$.

Preliminary calculations showed that the position of minimum energy always corresponded to an inner radius, r_α, of zero. The outer radius, r_β, was usually in the range 3-4 Å. All the results described here have been obtained by setting r_α to zero and adjusting r_β to give the minimum total energy.

The results are summarized in Table 1. Only the lower energy virtual orbitals are given in the cases of the larger basis sets. The gross features of the results are satisfactory. The molecular orbital energies are physically reasonable, there are always four bonding orbitals, and no more, and the total energy decreases as the basis set is expanded, though by an amount which suggests that we are using far from optimum basis sets.

The experimentally determined ionization potentials of S_4N_4 [29] are shown on the right of Table 1. One would expect a Jahn-Teller splitting from the 1*e* level, and this can be quite large; 0.7 eV in the case of methane for example [30]. It therefore seems reasonable to interpret the data in this way and it is seen that the agreement with experiment, if not striking, is quite acceptable for a model which contains no experimentally adjusted parameters; the only empirical element being the choice of model Hamiltonian at the outset.

The same might also be said of the comparison of the calculated excited state energies with electronic spectral data, Table 1. The *E* state has been unambiguously assigned from magnetic circular dichroism spectra [31], the other two probably correspond to

Table 1. Calculated electronic energy levels for S_4N_4[a]

Basis	1s1p1d				1s1p1d1f2s				1s1p1d1f2s2p				
ϱ_{N}		1.0	0.9	0.3		1.0	0.9	0.8		1.0	0.9	0.8	Experiment[b, c]
Orbital Energies	$1a_1$	−0.449	−0.445	−0.434	$1a_1$	−0.464	−0.464	−0.460	$1a_1$	−0.477	−0.478	−0.478	−0.361
	$1e$	−0.304	−0.306	−0.304	$1e$	−0.299	−0.299	−0.299	$1e$	−0.323	−0.316	−0.312	−0.316; −0.344
	$1b_2$	−0.180	−0.203	−0.221	$1b_2$	−0.200	−0.224	−0.244	$1b_2$	−0.193	−0.214	−0.252	−0.287
	$1b_1$	0.060	0.085	0.118	$1b_1$	0.071	0.102	0.142	$1b_2$	0.074	0.086	0.105	
	$2e$	0.253	0.251	0.259	$2e$	0.181	0.182	0.195	$2a_1$	0.147	0.152	0.212	
	$2b_2$	0.258	0.262	0.274	$2a_1$	0.252	0.262	0.284	$2e$	0.150	0.147	0.158	
Total energy		−2.729	−2.791	−2.894		−2.847	−2.910	−3.031		−2.921	−2.961	−3.052	
r_β/Å		3.30	3.29	3.27		3.25	3.23	3.19		4.21	4.12	3.50	
Singlet state energies	A_2	0.034	0.082	0.130	A_2	0.062	0.115	0.168	A_2	0.091	0.121	0.154	0.105A_2
	E	0.195	0.220	0.248	E	0.188	0.215	0.245	B_2	0.163	0.186	-	0.150A_2 or B_1
	A_1	0.244	0.271	0.301	E	0.232	0.243	0.265	E	0.187	0.201	0.227	0.179E
	E	0.247	0.264	0.283	B_2	0.236	0.267	-	E	0.188	0.216	0.248	
					A_2	-	-	0.290	A_1	0.204	0.228	0.253	
									A_2	-	-	0.276	

[a] All entries were calculated using five quadrature points. All energies in a.u.

[b] Ionization potentials; A. F. Orchard, unpublished data.

[c] Electronic spectra; R. Grinter, unpublished data.

forbidden transitions and must therefore be of A_1, A_2 or B_1 symmetry in D_{2d}. Thus the calculations fail to predict the second, low-intensity band except in the case of the largest basis set. If, as appears reasonable, we assume that this represents the "best" calculation then the agreement with the electronic spectral data is quite good for $Q_N = 1.0$. For the ionization potentials, however, a less even distribution of charge seems indicated.

2.2. Benzene

Our calculations on this molecule are summarized in Table 2. The molecular orbitals calculated with the present model lack the planar mode containing the six carbon atoms which characterizes the usual π-electron LCAO MOs. However, in other respects, the nodes perpendicular to the plane of the benzene ring in particular, the present functions bear a very close resemblance to them. As with S_4N_4, we again find the results physically reasonable and, as far as the orbital energies are concerned, in quite acceptable agreement with experiment for a theory with no experimentally adjustable parameters. The comparison with the *ab initio* calculations [32–34] is made not because we wish our model to be regarded as an *ab initio* method, but because those results show just how sensitive the π-electron orbitals of benzene are to the basis set chosen. Hay and Shavitt [32] used a double-ζ set of 72 contracted Gaussians to obtain the orbital energies quoted in Table 2. For the calculation of the π-electron excited states this basis was augmented by two diffuse π functions on each carbon atom and thousands of configurations were included in the configuration interaction calculation. Peyerimhoff and Buenker [33] used a basis set of approximate Hartree–Fock atomic orbitals expanded in terms of Gaussians. To increase the flexibility of the π-electron part of the wave function the $p\pi$ group functions were decomposed into a four-component short-range part and a one-component long-range part. This made little difference to the total energy but had a major effect on the composition of the π orbitals. Hay and Shavitt [32] report the same experience with their augmenting π functions.

Ermler, Mulliken and Clementi [34] used a large contracted Gaussian basis set with the addition of p- and d-type polarization functions on hydrogen and carbon respectively. They did not attempt calculations of the energies of excited states.

Comparison with experiment shows that, with regard to the orbital energies, the agreement is quite good, particularly in the case of the larger basis sets. The excited state energies however are uniformly too high, and, in the case of the triplets, their order does not correspond to the experimental sequence of energies. Closer inspection reveals that this latter problem is of a very fundamental nature since for several basis sets the B_{1u} and B_{2u} states are calculated to have the same energy, which is not in accord with experiment. This situation arises because the one-electron basis functions span the following irreducible representations in D_{6h} symmetry; $s - a_{1g}; p - a_{2u}, e_{1u}; d - a_{1g}, e_{1g2g}, f - a_{2u}, e_{1u}, e_{2u}, b_{iu}, b_{2u}$. The highest occupied and lowest unoccupied orbitals for all the basis sets considered are e_{1u} and e_{2g} respectively.

In $D_{6h} e_{1u} \times e_{2g} = B_{1u}, B_{2u}$ and E_{1u} and, in principle, the B_{1u} and B_{2u} states may have different energies. However, in the present model the electron repulsion operator which

Table 2. Calculated electronic energy levels for benzene[a]

						c		c	d	e	f	g
	Symmetry[b]	1*s*1*p*1*d*	1*s*1*p*1*d*2*s*	1*s*1*p*1*d*1*f*2*s*	1*s*1*p*1*d*2*s*2*p*2*d*	1*s*1*p*1*d*2*s*2*p*2*d*	1*s*1*p*1*d*1*f*2*s*2*p*	1*s*1*p*1*d*1*f*2*s*2*p*	*Ab inito*	calculations		Experiment
Orbital energies	$1a_{1g}$	−0.514	−0.529	−0.494	−0.530	−0.554	−0.499	−0.503	−0.505	−0.543	−0.501	−0.459
	$1e_{1u}$	−0.265	−0.268	−0.282	−0.321	−0.339	−0.328	−0.351	−0.340	−0.378	−0.337	−0.340
	$1e_{2g}$	0.207	0.192	0.241	0.173	0.099	0.185	0.180	*h*	0.097	0.119	
	$1a_{2u}$	0.310	0.290	0.316	0.207	0.175	0.215	0.190	*h*	0.302	*h*	
	$2a_{1g}$	0.481	0.365	0.433	0.238	0.274	0.279	0.324				
Total energy		−2.106	−2.109	−2.276	−2.430	−2.416	−2.422	−2.418				
r_β/Å		2.82	3.00	2.76	3.71	3.71	3.45	3.45				
State energies[i,j]	$^3B_{1u}$	0.189	0.184	0.214	0.235	0.171	0.242	0.274	0.141	0.152	*h*	0.143
	$^3E_{1u}$	0.189	0.181	0.225	0.242	0.171	0.235	0.279	0.183	0.191	*h*	0.173
	$^3B_{2u}$	0.189	0.184	0.217	0.235	0.171	0.242	0.275	0.257	0.270	*h*	0.206
	$^1B_{2u}$	0.238	0.232	0.283	0.279	0.215	0.293	0.317	0.183	0.191	*h*	0.184
	$^1B_{1u}$	0.238	0.232	0.283	0.279	0.215	0.293	0.317	0.281	0.297	*h*	0.232
	$^1E_{1u}$	0.344	0.321	0.384	0.336	0.314	0.360	0.394	0.307	0.346	*h*	0.257

[a] All entries except columns 5 and 7 were calculated using 5 quadrature points. Energies in a.u.

[b] The orbital symmetries are not the usual LCAO MO symmetries; see text.

[c] Results in these columns were calculated using 15 quadrature points.

[d] Ref. [32].

[e] Ref. [33].

[f] Ref. [34].

[g] Ionization potentials from: Edquist, O., Lindholm, E., Selin, L. E., Asbrink, L.: Chem. Phys. Letters **5**, 192, 609 (1970), state energies from the compilation of Hay and Shavitt.

[h] Values for these quantities not quoted.

[i] All singly excited states of B_{1u}, B_{2u} and E_{1u} symmetry were included in the configuration interaction.

[j] The B_{1u} and B_{2u} states are not always separated in our calculations; see text.

lifts the degeneracy between the four, one-electron $e_{1u} \rightarrow e_{2g}$ transitions has full rotational symmetry. Thus it cannot split states differing only in the sign of the z-component of their electronic angular momentum; $\pm 3 (\phi_u$ in $D_{\infty h})$ in this particular case. Only by introducing an electron repulsion term which is dependent upon the D_{6h} symmetry of the atomic cores can this degeneracy be lifted, as it is in the Pariser-Parr-Pople treatment of the π-electron structure of benzene for example.

The very high symmetry of the electron repulsion operator must give rise to problems of this type in any one-centre method and this does not appear to have been clearly recognized in the literature. Naturally, if the basis set forms part of a complete set, then by expanding it sufficiently results of any desired degree of accuracy may be obtained - within the limits of the HF approximation. But this constitutes another reason why one-centre basis sets have to be rather large if they are to give a good description of the system to which they are applied.

In our example, by adding *f* orbitals to the basis we can generate vacant orbitals of b_{1u} and b_{2u} symmetry which, through transitions to them from the occupied a_{1g} orbital, will give rise to B_{1u} and B_{2u} states of unequal energies. The effect can be seen in the results quoted in Table 2. However, the energy separation of the lowest B_{1u} and B_{2u} states is very small because the states with which they are interacting are much higher in energy. Clearly, a large amount of configuration interaction would be required to give good agreement with experiment.

From the results for S_4N_4 and benzene described above it might appear that, with the introduction of suitably chosen parameters, the theory might be capable of reproducing electronic properties with an accuracy of the same order as that of other semi-empirical methods. However, it is not our purpose to attempt such a process for two reasons. In the first case, there is already a wide range of semi-empirical methods available [35], although they tend to be restricted to first- and second-row elements. Secondly, and in our view more importantly, the particular systems which we have in mind, cage-type molecules and ions in general, are of such wide variety that it appears improbable in the extreme that any satisfactory parametrization could be found, except within very restricted classes; the boranes and carboranes, for example. Our intention is to explore the model more deeply, and to this end we now consider its application to problems where a much larger proportion of the valence electrons of a molecule require to be considered.

3. Systems in which it is Necessary to Treat All the Valence Electrons

In the cases of benzene and tetrasulphur tetranitride it appears quite acceptable to separate out a comparatively small number of valence electrons for special treatment. In the case of conjugated hydrocarbons this concept has been one of the most fruitful in the history of theoretical chemistry. But in trying to find a model for the effective description of the electronic structures of cage-type molecules it is not always possible to select such a group of electrons. A consideration of the tetrahedral phosphorus molecule, P_4, will highlight this problem, and will also serve to illustrate the ways in which the simple theory outlined above must be developed if it is to have any widespread applicability.

P_4 is a compact molecule with twenty valence electrons surrounding four cores of ten electrons each. Even though a formal structure of two-electron P-P bonds and lone pairs can be drawn it seems inconceivable that such a structure can truly represent the electronic structure of P_4 and one would expect extensive delocalization. Also, the six bond-pairs at the edges of the triangular faces would be expected to "spill over" into the centres of the faces, an effect which is found in *ab initio* calculations [36]. In brief, in our model all twenty valence electrons must be considered, and this is what we have done. The results are given in Table 3.

It is immediately apparent that there are far too few bonding orbitals. However, we observe that the number of bonding orbitals increases as the outer shell radius increases and this provides a clue to the understanding of the problem; it can be interpreted in two ways. Firstly, it may be due to the repulsion integrals giving too large a positive contribution to the orbital energies at the radius of minimum total energy. This could be caused by a failure of the model to include shielding of repulsions between valence electrons by the positively charged cores [37]. Alternatively, one might say that the fact that we get the correct number of bonding orbitals for a radius greater than that for minimum energy indicates an incorrect balance of one-electron attractive and two-electron repulsive terms. Again, an inadequate treatment of the atomic cores seems indicated.

The shortcomings of the present model with respect to its treatment of the core electrons are easily seen in the following analysis. In calculating orbitals for twenty electrons in the field of four cores, each with a charge of +5, we are effectively perform-

Table 3. Calculated energy levels for P_4[a]

		1*s*1*p*1*d*1*f*2*s*	1*s*1*p*1*d*1*f*2*s*2*p*	*ab initio* Calculation[b]
	Orbital energies			
	1a_1	−1.720	−1.742	−1.158
	1t_2	−1.508	−1.484	−0.772
	2a_1	−0.060	0.396	−0.458
	2t_2	0.182	0.469	−0.410
	1e	0.247	0.596	−0.385
	1t_1	0.704	1.106	0.061
	3a_1	0.818	1.230	-
	3t_2	1.071	1.506	0.066
	4t_2	-	1.654	-
Total energy		−33.377	−33.377	
r_β/Å		2.34	2.10	

[a] All entries calculated using five quadrature points. All energies in a.u.

[b] Ref. [36].

ing calculations on B_4 with the geometry of P_4. This has two consequences. Firstly, we know that if a tetrahedral molecule B_4 existed it would certainly have eight electrons which were highly localized in pairs around the boron nuclei, i.e. they would be boron 1*s* electrons. Our model must be very poor at reproducing the wave functions of such electrons. Secondly, the molecule cannot be in equilibrium unless the nuclei are allowed to move much closer together. Finally, by ignoring the core electrons we give our valence electrons too much space in which to move. This is clear from the fact that the radii for minimum energy given in Table 3 are only 2.34 and 2.10 Å, while the nuclei lie at 1.353 Å, from the centre.

It is clear that our model can only be extended to systems in which we require to handle fairly large numbers of valence electrons if we consider the core electrons much more explicitly than we have done so far. It is equally obvious that the model cannot treat these inner electrons directly since one-centre models are notoriously inadequate for reproducing highly localized off-centre electron density [38]. The pseudo potential theory, long known in solid-state physics but only comparatively recently applied to molecular problems, appears to be the ideal method for dealing with difficulties outlined above. This will be the subject of a second paper.

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Appendix A

Evaluation of Electron Repulsion Integrals

The repulsion double integrals are of two types:

$$I_u = \int_A^B f(x)dx \int_C^x g(y)dy \tag{A1}$$

$$Iv = \int_A^B f(x)dx \int_x^D g(y)dy \tag{A2}$$

Gaussian quadrature provides an accurate and comparatively simple means of evaluating these two integrals.

The following substitutions are made in the integral I_u to change the limits of the outer integration to zero to one:

$$\begin{aligned} x &= A + (B - A)p \\ f(x) &= f[A + (B - A)p] \equiv F(p) \\ dx &= (B - A)\,dp \end{aligned} \tag{A3}$$

so that

$$I_u = \int_0^1 [F(p)](B-A)\,dp \int_C^x g(y)\,dy$$

$$= (B-A) \sum_{m=1}^{NQP} R_m X_m(p_m) \tag{A4}$$

where p_m and R_m are the Gaussian quadrature nodes and weights respectively of an NQP-point set, and $X_m(p_m)$ is defined by Eq. (A5)

$$X_m(p_m) = F(p_m) \int_C^{A+(B-A)p_m} g(y)\,dy. \tag{A5}$$

The integral in (A5) can similarly be approximated by quadrature; the limits of this integration are changed to zero to one by the substitutions

$$y = C + [A + (B-A)p_m - C]\,q_n \tag{A6}$$

$$g(y) = g\{C + [A + (B-A)p_m - C]\,q_n\} \equiv G(p_m, q_n)$$

$$dy = [A + (B-A)p_m - C]\,dq.$$

So that

$$X_m(p_m) = F(p_m)[A + (B-A)p_m - C] \int_0^1 G(p_m, q_n)\,dq$$

$$= F(p_m)[A + (B-A)p_m - C] \sum_{n=1}^{NQP} R_n G(p_m, q_n) \tag{A7}$$

where q_n and R_n are the Gaussian quadrature nodes and weights respectively of an NQP-point set. Combining Eqs. (A7) and (A4):

$$I_u = (B-A) \sum_{m=1}^{NQP} R_m \cdot f[A + (B-A)p_m] \cdot [A + (B-A)p_m - C]$$

$$\cdot \sum_{n=1}^{NQP} R_n \cdot g\{C + [A + (B-A)p_m - C]\,q_n\}. \tag{A8}$$

The corresponding formula for I_v can be derived in a similar way; it is

$$I_v = (B-A) \sum_{m=1}^{NQP} R_m \cdot f[A + (B-A)p_m] \cdot [D - A + (A-B)p_m]$$

$$\cdot \sum_{n=1}^{NQP} R_n \cdot g\{A + (B-A)p_m + [D - A + (A-B)p_m]\,q_n\}. \tag{A9}$$

The accuracy of this type of linked quadrature is governed by the same factors that determine the accuracy of simple Gaussian quadrature [22]. Notably, since the integrand is replaced by a polynomial, the accuracy will depend upon the fidelity with which polynomials of degree $(2NQP + 1)$ can replace the two integrands $f(x)$ and $g(x)$.

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