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Buckyball Super-polyhedra

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The possibility of interlinking buckminsterfullerene molecules *via* σ-bonds to form novel nanostructures is considered. That is, each »node« of such a super-structure is itself a buckyball. Particular attention is directed to regular polyhedral nanostructures as well as the self-similar truncated icosahedral nanostructure. A systematic consideration of geometric constraints is presented, and an informative perturbative development of the π-MOs and their eigenspectra is made. A truncated icosahedral construction yields a buckyball buckyball, and iteration of this construction leads toward a buckyball fractal.

INTRODUCTION

The area of nanotechnology is currently of great interest.[1] Chemically the structuring of molecular frameworks becomes of central concern, so that there are several possibilities[2,3,4] for molecular »tinkertoy« sets. The C_{60} Buckminsterfullerene molecule[5] may itself be viewed as a highly symmetric »uniquely elegant« nano-ball. But moreover each buckyball may be viewed as a unique type of nano-socket component to be used as a building block in constructing larger nanostructures – here an important aspect of this uniqueness concerns the 60 equivalent positions from which to make external bonds, thereby allowing for the possibility of many different arrangements, to a much greater extent than for previously proposed molecular »sockets« (up to the complexity of cubane[2] and icosahedral[3] $-CB_{10}H_{10}C-$ units). Indeed buckyball dimers (with two adjacent tetrahedral sp^3-hybridized atoms on one buckyball σ-bonded to two like atoms on the other buckyball) have been considered theoretically,[6,7] and buckyball polymer chains (each buckyball

having a pair of sp^3-hybridized atoms on opposite sides of the ball) have been synthesized[8] and studied theoretically.[9] But more elaborate supercycle-containing arrays of interconnected buckyballs may be conceived, as we do here. Indeed along a similar line of reasoning a triangular net[10,11] of buckyballs has recently been proposed as a theoretical possibility. And there is some suggestion[12] and even evidence[7,13] that solid phases with inter-fullerene cycles are formed under suitable experimental high-pressure conditions. Indeed all these earlier works[7–13] focus on one type of interconnection, such as we consider here – though there are other possibilities.

To interconnect buckyballs into predesignated structures special attention needs to be taken to avoid radicaloid structures and strain. The radicaloid nature of a so-bonded buckyball may be simply estimated from an examination of the π-network of the remaining sp^2-hybridized atoms – clearly as a first criterion one must introduce only even numbers of sp^3-hybridized atoms. As regards strain the angles between the σ-bonds from a buckyball to its different neighbors need to be properly arrangable, and whether this can be done is but a matter of geometric examination. Further as we have noted earlier[14] with the introduction of (not too many) externally σ-bonded sp^3-hybridized atoms some absolute isotropic (Gaussian) curvature strain is relieved – and the more uniformly these sp^3-hybridized atoms are spread out the less the absolute anisotropic curvature strain tends to be.

Of the various possible predesignated structures those based on regular polyhedra and perhaps also the truncated icosahedron (of buckminsterfullerene itself) offer intriguing target structures. In these cases each buckyball in such a structure is equivalent, each being connected to an equal number ν of other buckyballs: $\nu = 3$ for the tetrahedron, cube, dodecahedron, and truncated icosahedron; $\nu = 4$ for the octahedron; and $\nu = 5$ for the icosahedron. This then is the problem proposed here: to determine which such superpolyhedra are constructible (comprehensively within indicated presumptions of little strain); to check for possible radicaloid behavior; and to indicate some few of the consequent features of the π-network eigenspectrum. The super-polyhedron constructibility conditions and numerical tests are addressed in section 2 (p. 521) and 3 (p. 523), respectively, while novel splitting patterns in the π-electron eigenspectrum are found in sections 4 (p. 524) and 5 (p. 528).

As a further extension of such super-structures, we apply (in section 6, p. 530) such ideas to the truncated icosahedron itself to generate a $(C_{60})_{60}$, and indicate some features of its π-spectrum in accord with the idea of sections 4 and 5. Next we seek to extend the whole constrution process using mth stage buckyballs as sockets to construct $(m + 1)$th stage buckyballs. Such continued iteration leads (as is seen in section 7, p. 532) toward a fractal dimension $D \approx 2.8775$. These icosahedral structures of course have I_h symmetry and local C_1 or C_σ symmetry for atoms.

SUPER-STRUCTURES

Ordinarily a pair of buckyballs is not to be exclusively connected together by a single σ-bond (in order to avoid reactive radicaloid structures), and here focus is directed to the case where interconnections between neighbor pairs of buckyballs are *via* pairs of bonds coming from neighbor pairs of atoms. We define a bond-directrix from one buckyball to a neighbor to be the line segment between their centers, and to avoid internal strain within the buckyballs the directrices are to be midway between the pair of bonds interconnecting the associated pair of buckyballs, as in Figure 1. Thence one seeks the ideal angles between different possible pairs of directrices to see which might accommodate to the ideal angles of the overall superpolyhedra under construction. A buckyball geometry can be obtained by truncation of an icosahedron. By choosing its three orthogonal two-fold axes to lie along the Cartesian axes, we have the coordinates of the icosahedron's twelve vertices: $\pm(\tau,1,0)\rho$, $\pm(0,\tau,1)\rho$, $\pm(1,0,\tau)\rho$, $\pm(\tau,-1,0)\rho$, $\pm(0,\tau,-1)\rho$, and $\pm(-1,0,\tau)\rho$ where 2ρ is the length of its edges and $\tau = \sqrt{5} + 1)/2$. To arrange C_{60} vertices with a distance d_p along a bond separating a pentagon and hexagon, the truncation places an atom d_p from each icosahedron apex with a distance d_h between the pairs of vertices so placed on each icosahedron edge – so that $2\rho = 2d_p + d_h$, and thereby determining the buckyball's coordinates.[15] Accordingly, the possible angles are listed in Table I for the 48 symmetry inequivalent pairs of directrices. Each directrix appearing there is labelled by the bond it bisects, each bond label being given in terms of its two component sites, which in turn are identified by the numbering of Figure 2. Also in Table I each bond (providing a directrix label) is identified as of type p-h or h-h as the bond occurs at the fusion of a pentagon with a hexagon or of a hexagon with a hexagon. Notably the angle between directrices (unless both are of type h-h) is in general not determined by the icosahedral symmetry of the buckyball, unless a choice is made for the bond lengths – the answers seem to be but slightly sensitive for reasonable ratios of the two bond lengths, so that we here choose all of the bond lengths equal in column 3 for directrix angle ϕ, and experimental results[16] in column 4 (ϕ') for corresponding angles. It is seen

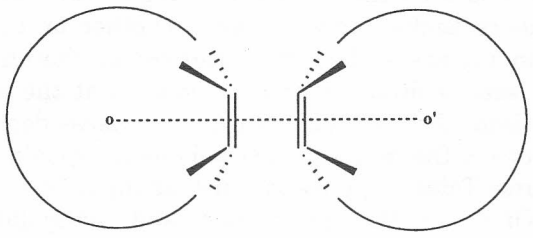

Figure 1. The directrix between the pair of bonds interconnecting the associated pair of buckyballs, with centers o and o'.

TABLE I

The directrix angles for equal (ϕ) and experimental (ϕ') bond lengths

h-h	h-h	$\phi = \phi'$
	(2-12)	36.00
	(3-15)	60.00
	(13-14)	72.00
(1-9)	(16-7)	90.00
	(32-33)	108.00
	(34-35)	120.00
	(50-51)	144.00
	(52-60)	180.00

h-h	h-p	ϕ	ϕ'
	(1-2)	20.55	20.42
	(2-3)	39.68	39.85
	(11-12)	41.81	41.53
	(3-4)	48.19	48.47
	(12-13)	54.64	54.61
	(13-30)	72.00	72.24
	(14-15)	74.36	74.09
(1-9)	(15-16)	80.41	80.24
	(14-33)	90.00	90.00
	(16-34)	99.59	99.76
	(33-34)	105.64	105.91
	(31-32)	108.00	107.76
	(32-50)	125.36	125.39
	(35-36)	131.81	131.53
	(49-50)	138.19	138.47
	(35-51)	140.32	140.15
	(51-52)	159.45	159.58

h-p	h-p	ϕ	ϕ'
	(2-3)	19.19	19.51
	(1-2)	31.29	31.83
	(15-16)	36.00	35.52
	(14-15)	41.11	40.84
	(12-13)	54.07	53.90
	(11-12)	60.20	60.24
	(9-10)	66.80	66.86
	(13-30)	70.72	70.79
	(11-29)	79.35	79.71
	(35-36)	83.62	83.05
	(10-26)	85.31	85.68
(3, 4)	(31-32)	94.69	94.32
	(25-26)	96.38	96.95
	(32-50)	100.65	100.26
	(31-48)	109.28	109.21
	(27-28)	113.20	113.14
	(28-47)	119.80	119.76
	(27-45)	125.93	126.10
	(46-47)	138.89	139.16
	(45-46)	144.00	144.48
	(59-60)	148.71	148.17
	(58-59)	160.81	160.49
	(57-58)	180.00	180.00

from the truncation construction that the directrix angles between h-h and h-h are independent of the bond lengths.

From Table I it is seen that only a few angles are appropriate for any one of the polyhedra under consideration. Whether or not the additional (v–2) directrices in any one of these few cases can be chosen to accommodate to the v-member sets of directrix angles required at the buckyball is now treated by inspection, thence giving a comprehensive determination of all possible realizations of the desired super-polyhedra (within the assumptions indicated). Of course Table I applies in constructing different possible super-lattices as well. Of note is the linear chain[9] and triangular lattice.[10,11] But there are other possibilities too.

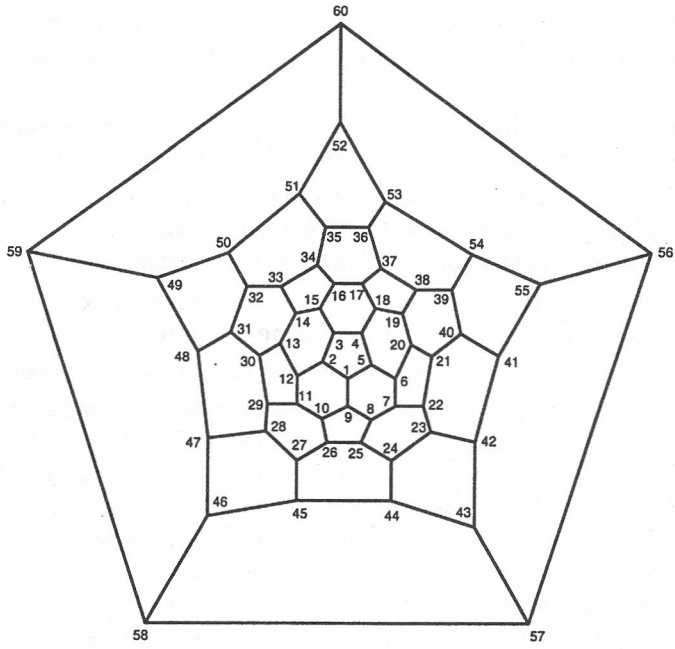

Figure 2. The site numbering here utilized for the buckyball.

SUPER-POLYHEDRA

The different super-polyhedra are designated via the choice of n directrices within a component buckyball. Choices for such ν-member sets (for degree-ν super-polyhedra) of directrices in turn being indicated by bonds as in-

TABLE II

Graph-theoretic invariants for each buckyball in different super-polyhedra

Polyhedra	Bond positions	π-Fragment symmetry	Hückel		VB-related			
			gap/β	REPE/β	K	K_6	K_{10}	REPE
Cube	1-9;16-17;30-31	C_3	0.7970	0.04939	1204	9232	4212	0.1412
Dodeca-hedron	1-9;32-33;38-39	C_{3v}	0.5615	0.04787	1342	9152	4404	0.1266
Icosa-hedron	7-8;10-11;13-14; 16-17;19-20	C_{5v}	0.4989	0.03750	213	1050	510	0.0990
»Tetra-hedron«	3-4;11-12;14-33	C_3	0.3556	0.02812	152	636	408	0.0819

dicated in Table II, where also we report various graph-theoretic invariants for the remnant π-networks of 60–2v vertices. These graph-theoretic invariants include:

- the count K of Kekulé structures (»dimer covering« representing π-electron pairing patterns), done by way of Kasteleyn's method;[17]
- the conjugated-circuit counts K_c for circuits of size c (K_c/K being the average number of c-circuits with alternating double and single bonds), done by way our extension[18] of Kasteleyn's method;
- the tight-binding (Hückel) π-electron resonance energy per π-center (with our parameterization[19] of earlier schemes[20]); and
- the Hückel HOMO-LUMO gap (in units of the electron-hopping integral β).

It is seen that all of the π-network fragments so arising give nonradicaloid species, both as judged by the existence of Kekulé structures (or double-bond pairing patterns) and as judged by the existence of the nonzero HOMO-LUMO gaps. By inspecting the directrix angles, it is found that a super-cube, a super-dodecahedron, and a super-icosahedron can be built such that there are internal strain-free connections between adjacent buckyballs. The angles between directrices of h-h and h-h types do not depend on the bond-length ratio of h-h/h-p as indicated in Table I. These three polyhedra may be derived from »localized« 1,2-addition across h-h bonds, though for (hydrogenation of) a single buckyball 1,2-addition produces the thermodynamically most favored isomer at all levels of calculation[21] and experimental observation.[22] From the resonance energy per electron (REPE) under Hückel (tight-binding) MO and resonance-theoretic frameworks, the cube is the most stable while the icosahedron where there are 5 h-h π-bonds destroyed in forming the super-polyhedron is the most unstable. These are related to the results[23] for $C_{60}H_n$. For further comparison, we also construct an (only slightly) imperfect »tetrahedron« having directrix angles between two h-p bonds strained from $\approx 60.2°$. The REPE and HOMO-LUMO gap indicate that it is a somewhat less favored structure both kinetically and thermodynamically. Notably four suitably oriented directrices to form a regular octahedron were not found.

In Figure 3 we show an example of a buckyball polyhedron based on the cube. The geometry is optimized by using the SYBYL molecular force field, which yields similar interball bond lengths to those of tight-binding dynamics.[11] Notably in the regions of interconnection between buckyballs there is distortion to lessen the interaction between the π-networks of different component buckyballs, thereby suggesting a perturbative approach.

INTER-π-NETWORK INTERACTIONS

The results of the preceding section develop the π-electron spectra of each buckyball as through there is no interaction between the π-networks

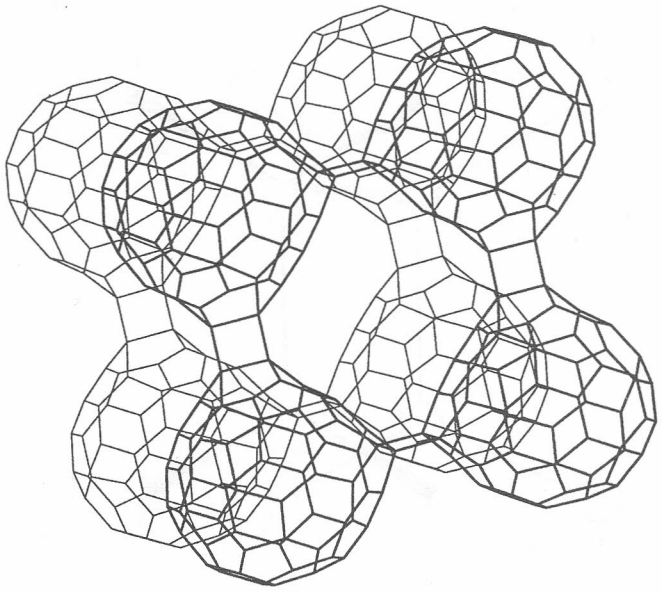

Figure 3. An example of a buckyball polyhedron based on the cube.

of different buckyballs. To correct for this approximation one could do a full-blown quantum-chemical computation on each full superpolyhedron. But some interesting insight is obtained if instead one treats the problem at a simple perturbative level. To this end we consider the region of bonding between two adjacent buckyballs, with atoms a and b of one buckyball σ-bonded to atoms a′ and b′ of an adjacent buckyball. See Figure 4 where also we indicate the four π-centers 1, 2, 3, 4 adjacent to a, b on one buckyball as well as 1′, 2′, 3′, 4′ adjacent to a′, b′ on the other buckyball. First evidently there will be some direct coupling between i and i' measured by a resonance (or electron-hopping) integral β'. Next there will be some coupling between each of the indicated π-orbitals on a buckyball and the σ-bonding and σ*-antibonding orbitals involved in the interconnection of the two buckyballs. The resonance-integral coupling to the σ-bonding orbital is identified as β'', and to a first approximation the coupling to the σ*-antibonding orbital is of the same magnitude but with correlated signs as indicated in Figure 5.

Now with these basic resonance integrals in hand we pursue a degenerate perturbation treatment. Each buckyball is viewed to have a zero-order π-orbital spectrum with no coupling between buckyballs. Since each buckyball in the superpolyhedron (of any regular or semiregular type) is equivalent, these zero-order eigenvalues are degenerate. If there is no additional degeneracy (between π-MOs of a single buckyball component with sp^3-hybridized centers deleted), then the treatment is most straightforward – and

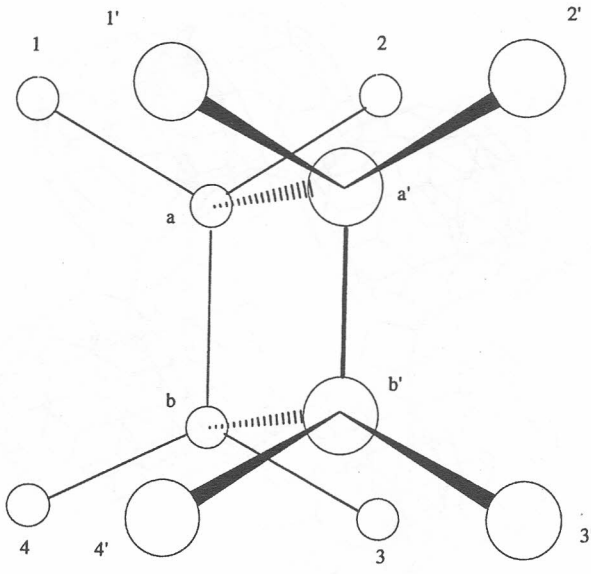

Figure 4. Arrangement and labelling at and near the interconnecting sites of two buckyballs.

this we now presume, delaying the case with internal degeneracy (as actually also occurs) to the next section. Then for a regular superpolyhedron with n buckyballs each buckyball is equivalent, so that each π-energy without internal degeneracy is n-fold degenerate. Degenerate perturbation theory then may be implemented through effective Hamiltonians each defined on an n-dimensional zero-order eigenspace. With H_0 and V the zero-order

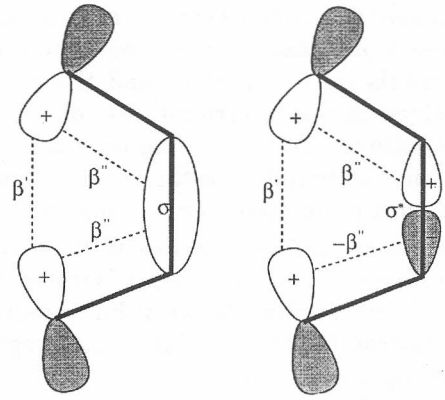

Figure 5. Labelling of the »resonance integrals« coupling the π-orbitals of two neighboring buckyballs.

Hamiltonian and the perturbation, respectively, the standard result for the effective Hamiltonian through second-order is

$$\mathcal{H} = O(H_0 + V + V\frac{O^-}{\varepsilon_0 - H_0}V)O \tag{1}$$

where O is the projector onto the zero-order eigenspace of energy ε_0, while $O^- = 1 - O$. The β''-couplings give no contribution to the first-order term OVO (since they do not couple between π-orbitals), but they do make a contribution in the second-order term. The β'-couplings which we imagine are weaker than β''-couplings make a contribution to OVO but are here neglected in the second-order term.

To set up the effective Hamiltonian $\mathcal{H}$ we now consider its matrix elements. First the only diagonal part of less than second-order is

$$OH_0O = \varepsilon_0 1 \tag{2}$$

Next the only off-diagonal part which arises in the already indicated approximations is between nearest neighbor buckyballs. Thus letting

$$\psi = \sum_i c_i \chi_i \quad \text{and} \quad \psi' = \sum_i c'_i \chi'_i \tag{3}$$

denote the degenerate zero-order π-MOs on two adjacent buckyballs, we have

$$\langle \psi | OVO | \psi' \rangle = \langle \psi | V | \psi' \rangle = \beta' \sum_i^4 c_i c'_i \tag{4}$$

(with the notation of Figure 4). Further the β'' part of the second-order term is

$$\langle \psi | OV'' \frac{O^-}{\varepsilon_0 - H_0} V'' O | \psi' \rangle =$$

$$[(c_1 + c_2)(c'_1 + c'_2) + (c_3 + c_4)(c'_3 + c'_4)](\beta'')^2 [\frac{1}{\varepsilon_0 - \varepsilon_\sigma} - \frac{1}{\varepsilon_0 - \varepsilon_{\sigma^*}}] \tag{5}$$

where ε_σ and ε_{σ^*} are the energies of the σ- and σ^*-orbitals between the two (primed and unprimed) buckyballs. Now for all the constructions of Table II (and later of Table IV) each site i of Figure 4 turns out to be equivalent to site i', so that $c_i = c'_i$. Further summing (4) and (5) we obtain the total coupling element between neighboring buckyballs as

$$B = \beta'' \sum_i^4 c_i^2 + (\beta'')^2 [(c_1 + c_2)^2 + (c_3 + c_4)^2][\frac{\varepsilon_\sigma - \varepsilon_{\sigma^*}}{(\varepsilon_0 - \varepsilon_\sigma)(\varepsilon_0 - \varepsilon_{\sigma^*})}] \tag{6}$$

Farther-neighbor coupling occurs only in higher orders of perturbation theory than included here.

Thus there results a simple description of the perturbed form of the eigenspectrum. Each nondegenerate π-level of a single buckyball component is split up into a n-fold manifold of levels with a pattern characteristic of the particular n-apex regular polyhedron under consideration. That is, the pattern is that of the eigenvalues to the (graph-theoretic) adjacency matrix for the regular polyhedron. The strength of the interaction governing the scale of the splitting is different for each zero-order level, and is given in equation (6). An example of such treatment will be given in the following section.

The treatment here applies to extended structures as well as polyhedral ones. Thus for a polymer chain[8,9] of buckyballs, there should be a 0-order pattern for a C_{2v} C_{56} graph with each (typically non-degenerate) level should show a fine splitting into a linear-chain (polyacetylene-like) band. Indeed such can be percieved to some extent in Springborg's[9] computated energy-level density plots, though a higher resolution might help.

INTERACTIONS WITH INTERNAL DEGENERACY

It remains to consider the modification to the results of the preceding section when there is 0-order degeneracy of π-levels within individual buckyball components. In fact, this must rather frequently happen since (as seen from Table II) the symmetry groups often are such as to give 2-dimensional irreducible representations (or pairs of complex-conjugate 1-dimensional co-representations) and consequent 2-fold internal degeneracies, whence the degenerate perturbation-theoretic Hamiltonian matrix becomes doubled in dimensionality.

As an example consider the case of C_3 or C_{3v} symmetry groups. Then there will be degenerate π-MOs ψ_+ and ψ_- transforming under rotation by $2\pi/3$ as

$$C_3\psi_\pm = \eta^{\pm 1}\,\psi_\pm \tag{7}$$

where $\eta \equiv e^{i2\pi/3}$. Then for an n-apex superpolyhedron one has in 0-order a $2n$-fold degeneracy (assuming no further »accidental« degeneracy). The $2n$-dimensional degenerate perturbation-theoretic matrix problem still has nonzero matrix elements just between adjacent buckyballs, but there is some question as to how to develop the problem so as to manifest its full symmetry. First noting that $\psi_+^* = \psi_-$, we may obtain a set of real 0-order eigenvectors

$$\psi_a \equiv (\psi_+ + \psi_-) / \sqrt{2}$$

$$\psi_b \equiv C\psi_a = (\eta\psi_+ + \eta^*\psi_-) / \sqrt{2} \tag{8}$$

$$\psi_c \equiv C\psi_a = (\eta^*\psi_+ + \eta\psi_-) / \sqrt{2}$$

Evidently these are symmetrically equivalent, though linearly dependent since

$$\psi_a + \psi_b + \psi_c = 0 \tag{9}$$

Then each of ψ_a, ψ_b and ψ_c should have larger magnitude amplitudes near one corresponding interconnection region to a neighboring buckyball. Thence the interaction matrix elements between adjacent pairs of buckyballs can be developed in a systematic fashion, following the approach of the preceding section. But in place of a single matrix element B as in (6) between ψ and ψ' in two buckyballs I and I′ there will be an array of matrix elements between ψ_a, ψ_b and ψ_c on I ψ'_a, ψ'_b and ψ'_c on I′. See Figure 6. Then the different matrix elements are

$$B_{xy} = B_{yx} = \beta' \sum_i^4 c'_{xi}\, c_{yi} +$$

$$(\beta'')^2 [(c'_{x1} + c'_{x2})(c_{y1} + c_{y2}) + (c'_{x3} + c'_{x4})(c_{y3} + c_{y4})] \frac{\varepsilon_\sigma - \varepsilon_{\sigma^*}}{(\varepsilon_0 - \varepsilon_\sigma)(\varepsilon_0 - \varepsilon_{\sigma^*})} \tag{10}$$

where the c_{xi} and c'_{xi} are amplitudes for ψ_x and ψ'_x (x = a, b, and c). Because of (9) there are just three independent matrix elements here, say B_{aa}, B_{bb}, and B_{ab}.

Thus again there results a still somewhat simple description of even this portion of the eigenspectrum. Each E-level of a single buckyball component is split up into a $2n$ manifold of levels with a pattern characteristic of a »decoration« of the n-apex regular polyhedron under study, the decoration involving the replacement of each of the n-apices by 3 new graph vertices with interconnections as in Figure 6. That is, the pattern is that of the generalized eigenvalue problem

$$\boldsymbol{A}^{dec}\boldsymbol{C} = \lambda \boldsymbol{S}^{dec}\boldsymbol{C} \tag{11}$$

where $\boldsymbol{A}^{dec}$ is the weighted adjacency matrix for the decorated graph with the weights being as indicated in (10), and $\boldsymbol{S}^{dec}$ is an overlap matrix associated with the linear dependence of (9). That is, the sole nonzero elements of $\boldsymbol{S}^{dec}$ are 1 on the diagonal and –1/2 between distinct ψ_x, ψ_y associated to the same buckyball. Further the n eigenvalues of 0 associated to the n 0-eigenvalue

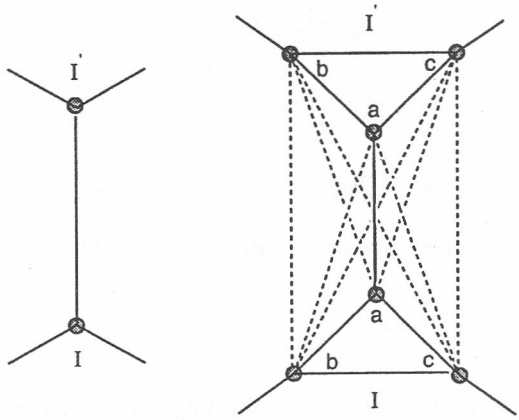

Figure 6 Decoration construction, replacing each vertex of a superpolyhedron by 3 new vertices, as well as a corresponding edge replacement as indicated.

eigenvectors to S^{dec} are recognized to be due to the linear dependence, and so are discarded from the level pattern. The advantage to using (11) including this linear dependence »nuisance« is that the distinct matrix elements are few and this form explicitly manifests the geometric symmetry of the superpolyhedron.

Finally the treatment of the icosahedron superpolyhedron with C_{5v} symmetry is similar. A decoration replacing each apex of the icosahedron by 5 vertices arises. Further too the perturbative approach of this and the preceding section should be applicable in constructions based on other sockets, *e.g.*, the $-CB_{10}H_{10}C-$ units of Ref. 3.

BUCKYBALL BUCKYBALLS

There is growing interest in the realization and development of well-defined nanostructures which are »self-similar«. Here we view a buckyball as a type of nano-socket component to be used in constructing a larger superbuckyball $(C_{60})_{60}$, which might be called the buckyball buckyball (just as we might term the structure of Figure 3 a buckyball cube). But in turn this might be used in construction an even larger super-superbuckyball $((C_{60})_{60})_{60}$ *etc.* Again, the interconnections between neighbor pairs of buckyballs are via pairs of bonds coming from neighbor pairs of atoms as discussed in section 2 (p. 521). According to the directrix angles shown in Table I, an infinite sequence of self-similar super-buckyballs can be constructed ideally (internally strain-free) step by step. But we delay consideration of these higher-order iterations to section 7 (p. 532).

For the first super-buckyball $(C_{60})_{60}$, the three bonds for inter-connections are, for example, 16-17; 22-23; and 28-29, where two of the angles between these three bonds are 120° and one is 108°. For this stage we have the simplest circumstance (with no symmetry-mandated internal degeneracies) and thus can seek to treat inter-π-network interaction as described in section 3 (p. 523). This structure is that of 60 buckyballs locating at the vertex positions of an (enlarged) truncated icosahedron. We estimate[23] $\beta' \approx 0.1\,\beta$, $\beta'' \approx 0.3\,\beta'$, $\varepsilon_\sigma \approx \alpha + 2.5\,\beta$, $\varepsilon_{\sigma*} \approx \alpha - 2.5\,\beta$ and $\alpha \approx 0.5\,\beta$ and proceed *via* (6). The well-known[24,25] truncated-icosahedron splitting pattern occurs with each level more finally split over a range $\sim \pm 3B_\xi$ on either side of the 0-order level. The non-degenerate levels may repeat this same pattern on a finer scale (as discussed in section 4), while the symmetry-degenerate[25] levels yield a related fine-splitting (as discussed in section 5). But since the argu-

TABLE III

Splitting parameters for the buckyball buckyball

ξ	ε_ξ	B_ξ	Entry	ξ	ε_ξ	B_ξ	Entry
1	–2.862	0.0333	Yes	28	0.129	–0.0106	Yes
2	–2.712	0.0039	Yes	29	0.309	–0.0170	No
3	–2.596	0.0141	No	30	0.343	–0.0009	No
4	–2.550	0.0167	No	31	0.488	0.0081	Yes
5	–2.302	–0.0056	Yes	32	0.687	0.0086	Yes
6	–2.213	0.0054	Yes	33	0.815	0.0074	No
7	–2.182	–0.0003	Yes	34	0.830	0.0088	No
8	–2.027	0.0118	Yes	35	0.944	0.0446	No
9	–1.898	0.0034	Yes	36	0.986	0.0048	No
10	–1.728	0.0006	Yes	37	1.333	–0.0098	Yes
11	–1.585	–0.0076	No	38	1.370	0.0017	Yes
12	–1.571	0.0002	No	39	1.414	0.0045	Yes
13	–1.530	0.0061	Yes	40	1.486	–0.0008	No
14	–1.506	–0.0003	Yes	41	1.504	–0.0069	No
15	–1.355	–0.0071	Yes	42	1.584	–0.0013	No
16	–1.199	0.0013	Yes	43	1.595	–0.0037	No
17	–1.000	–0.0018	No	44	1.693	0.0129	No
18	–1.000	–0.0129	No	45	1.761	0.0379	No
19	–1.000	–0.0121	No	46	1.954	0.0644	No
20	–0.935	0.0015	No	47	1.970	0.0267	No
21	–0.894	–0.0204	No	48	2.241	–0.0004	No
22	–0.892	–0.0005	No	49	2.304	–0.0721	No
23	–0.701	0.0018	Yes	50	2.334	–0.0046	No
24	–0.679	–0.0027	Yes	51	2.553	–0.0026	No
25	–0.585	0.0001	No	52	2.577	–0.0086	No
26	–0.567	–0.0102	No	53	2.601	–0.0034	No
27	–0.345	0.0012	Yes	54	2.606	–0.0037	No

ments of section 4 and 5 are based on perturbation theory the predicted quantitative details can fail if the 0-order levels are overly close together compared to the induced (perturbative) splittings. Thence we check for this, marking the entry in Table III with »No« to indicate such failure – otherwise we mark the entry »Yes«. Notably several entries seem to need further corrections – perhaps most prominently the three »accidentally« degenerate levels at $\varepsilon_0 = -\beta$ – a value for Hückel-orbital energy where degeneracy frequently occurs for »non-symmetry-related« but understood reasons.[25] It is seen that the level-splitting patterns are predicted to be nonoverlapping for somewhat less than half the 0-order π-levels. Notably this nonoverlapping occurs more frequently for occupied than unoccupied π-levels,as may be anticipated from the factor $[(\varepsilon_\xi - \varepsilon_\sigma)(\varepsilon_\xi - \varepsilon_{\sigma^*})]^{-1}$ in (5) upon noting that ε_{σ^*} is more centrally located in the unocccupied-level range than ε_σ is in the occupied level range. But even when the splitting patterns interpenetrate one may anticipate that what often results appears much like a superposition of the different subspectra, because the states arising from different zero-order eigenspaces remain quite noninteracting over all but ≈4 (out of 60) sites of a buckyball.

THE BUCKYBALL FRACTAL

As already suggested we seek to repeat (over and over) the buckyball super-construction our considerations of the angles for diretrices indicating no interball (or inter super-ball) strain. For the next super-superball $((C_{60})_{60})_{60}$, we shall select 6 buckyballs from within each superball component to connect to its neighbors in the same way, and these 6 buckyballs each have $\nu = 4$ bond regions for interconnections, say, 16-17; 22-23, 28-29; and 52-60. This type of buckyball is identified as $C_{60}(4)$, while those with just $\nu = 3$ inter-connecting bond regions (as in the preceding paragraph) are identified as $C_{60}(3)$. Therefore, each superball contains two types of components: $C_{60}(3)$ and $C_{60}(4)$. For the $(m+1)$th stage ball, the numbers of π-centers for $C_{60}(3)$ and $C_{60}(4)$ in the corresponding superball may be developed in much the same manner to obtain them recursively from the mth stage numbers:

$$\nu_3^{(m+1)} = 60\ (\nu_3^{(m)} - 3 \cdot 2^m)$$

$$\nu_4^{(m+1)} = 60\ (\nu_4^{(m)} + 3 \cdot 2^m) \tag{12}$$

Solution of these recursions, with the requisite initial conditions, gives

$$\nu_3^{(m+1)} = \frac{26}{29}\, 60^{(m+1)} + \frac{180}{29}\, 2^m$$

$$\nu_4^{(m+1)} = \frac{180}{29}\,(60^m - 2^m) \tag{13}$$

TABLE IV

Graph-theoretic invariants for buckyball components in higher-level buckyballs

	Bond positions	Hückel		VB-related			
		gap/β	REPE/β	K	K_6	K_{10}	REPE
C_{60}	–	0.7566	0.04594	12500	83160	59760	0.1200
C_{60} (3)	16-17;22-23;28-29	0.4735	0.04834	1161	7756	4278	0.1270
C_{60} (4)	16-17;22-23;28-29;52-60	0.4928	0.04904	601	4148	1710	0.1300

The various graph-theoretic invariants for the remnant π-networks of $60 - 2v$ vertices now are given in Table IV. The results via both Hückel MO and resonance theory pictures indicate that all structures at each stage are nonradicaloid and thermodynamically favorable. To obtain the distance d_m between the centers of mth stage buckyballs in an $(m+1)$th stage buckyball consider the length of the long horizontal line in Figure 7. Letting r_m denote the radius of the mth stage buckyball (from its center to the center of an $(m-1)$th stage ball) we see that

$$d_m = \sqrt{r_m^2-(d_{m-1}/2)^2} + d_{m-1} + \sqrt{r_m^2-(d_{m-1}/2)^2} \tag{14}$$

But from Figure 7, one sees that r_m and d_{m-1} are just the (circum) radius and an edge length for the polyhedron. Then by way of the truncation construction for the semiregular case one may obtain

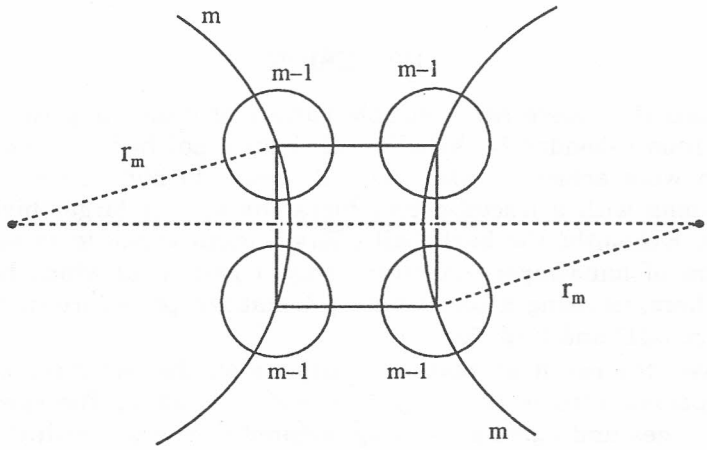

Figure 7 Arrangement considered for equation (8). Here two mth stage buckyballs have surfaces containing $(m-1)$th stage buckyballs as indicated. The lengths of the sides of the solid-lined square are d_{m-1}.

$$r_m = \sqrt{\tau+10/9}\, d_{m-1} \text{ (where } \tau = (\sqrt{5}+1)/2) \text{ so that}$$

$$d_m = \{1+2\sqrt{\tau+31/36}\}\, d_{m-1} \tag{15}$$

and

$$d_m = \{1+2\sqrt{\tau+31/36}\}^{m-1}\, d_1 \tag{16}$$

where d_1 is a first-stage interatomic distance (which is a suitable average since in fact the first stage is not precisely semiregular).

Now the iteration of the buckyball construction leads toward a fractal structure.[27] Granted the description[5] of the buckyball as »uniquely elegant«, surely too this fractal must be »uniquely elegant«. The fractal dimension is

$$D = \lim_{m\to\infty} \frac{\log \nu^{(m)}}{\log d_m} = \frac{\log 60}{\log\{1+2\sqrt{\tau+31/36}\}} \approx 2.8775 \tag{17}$$

which of course is a fundamental geometro-architectural characteristic. It or related dimensions also enter into various[28,29] physico-chemical spectral properties. The energy-level splitting considerations of section 4 (p. 524) and 5 (p. 528) still apply, though there are separate 0-order manifolds associated to the $\nu = 3$ and $\nu = 4$ buckyball. Further the buckyball-buckyball levels should be even more finely split upon formation of the buckyball buckyball buckyball (with somewhat similar consideration applying) – and indeed there should be a hierarchy of ever finer splittings on proceeding to ever higher stages, with[29] the splitting strength falling off in an exponential fashion. But this and other fractality manifestations are left to future work.

CONCLUSION

It is seen that there are a sizable variety of interesting constructions composed from σ-bonded buckyballs. All regular polyhedra other than the octahedron were achieved. Also the self-similar buckyball buckyball was achieved along with a fractal-potent hierarchy of ever larger higher-stage buckyballs. Evidently, the buckyball offers a quite versatile socket for the construction of nano-super-structures, only a portion of which have been identified here, utilizing a somewhat systematized procedure (indicated in section 2 (p. 521) and 3 (p. 523)).

Moreover, the result of inter-cage coupling on the π-electron eigenspectrum is elucidated (in section 5 (p. 528) and 6 (p. 530)). The spectrum for individual cages undergoes a splitting dictated by the polyhedral structure of the superpolyhedron into which the individual cages are placed.

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SAŽETAK

Buckminsterfullerenski supra-poliedri

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Razmatrana je mogućnost međusobnog spajanja molekula buckminsterfullerena σ-vezama u nove nanostrukture. Naročita je pažnja usmjerena na pravilne poliedarske nanostrukture i fraktalne krnje ikozaedarske nanostrukture. Sustavno su razmotrena njihova geometrijska svojstva, a račun smetnje primijenjen je na njihove π-molekulske orbitale i vlastite vrijednosti. Slaganje krnjih ikozaedarskih struktura daje buckminsterfullerenski buckminsterfulleren, a ponavljanja takvog slaganja daju fraktalne buckminsterfullerenske nanostrukture.