

物理学咬文嚼字之十二 各具特色的碳异形体

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翻译 从原作的终点出发.

——李玉民

Carbon, in fact, is a singular element...

——Primo Levi *The Periodic Table*

龙为中华图腾,象征吉祥.龙的形象是个典型的杂集诸种动物灵性与特长的概念.其子息,不能如龙本身那样集众长于一身,于是就别具一格起来,是以民间有“龙生九子,各有所好……”的说法(见《杨慎外集》).此说法,盛于明代.一说龙之九子,曰赑屃(龟像)、曰螭吻(鸱吻、鸱尾.蜥蜴像)、曰蒲牢、曰狴犴(宪章.虎像)、曰饕餮(狼像)、曰蚣蝮、曰睚眦(豺像);曰狻猊(狮像)、曰椒图(螺蚌像).当然,众口相传的东西,难免有讹错变种.出现在其他龙之九子版本中的名称还包括囚牛(黄色小龙)、嘲风(狗像)、负负(身似龙,雅好斯文)、螭首、麒麟、朝天吼、貔貅,等等.龙生九子的传说,可能源于人们对日常生活中对称性破缺现象的臆想(意象)式直观描述,类似的还有“十个手指有长短”、“一棵树的果子有酸有甜”等说法.这里涉及的事物,都是树、手、龙之类的复杂体系,其子系统表现出多样性并不令人意外.然而天机难测,这样有趣的现象,竟然由一种元素在单质物质的层面上就给敷演出来了.这种元素就是碳.

元素碳,其英文 carbon 来自拉丁语 carbo, carbonis, 燃烧的意思.碳元素在地球上的自然存在 coal, charcoal (to burn 燃烧), 就是我们中文中的炭(煤炭,焦炭,木炭),其作为可燃物,早已为史前人类所认识.实际上,对炭这种天然产品的认识,中外是一样的.中文的“炭”字字面上乃“烧木余也”(《说文》).唐朝白居易就有“卖炭翁,伐薪烧炭南山中”的诗句,说明唐朝时伐薪烧炭已是一项商业化的生产活动.可见越是对自然的、历史古老的事物,人类的认识就越是统一!“碳”字,是20世纪初西学渐进时中国学者徐寿(1818—1884,江苏人)新创

的,大概添加“石”旁是想表明炭是非金属矿物类,以后与元素 carbon 有关的科学点的词汇都被要求写成“碳”字.不过,笔者怎么看怎么觉得多此一举,它不仅科学上是错误的,还徒增文字辨识上的麻烦.《咬文嚼字》杂志社把碳-炭列为2007年度最容易混淆的十个字之一,举例就包括有人常把“碳酸饮料”写成“炭酸饮料”,把“炭烧咖啡”写成“碳烧咖啡”,等等.注意到把元素名称和实体名称非要用两个汉字区别开来的,碳-炭怕是独此一家,大家也就理解了为什么会容易发生混淆,因为并没有严格的定义可将两者区分开.到底是“炭黑(lampblack)”还是“碳黑”,为什么干电池里是炭棒(炭做的棒棒),接上高电压的炭棒怎么就成了碳棒,中间的放电就叫碳弧(请注意炭棒导电的事实!)?谁又比谁科学了不成(不会是嫌焦炭太黑,金刚石不愿认亲兄弟吧)?笔者建议(我知道人微言轻的道理,权当白说),应把“碳”字放弃掉.作为对这一建议的响应,下文中笔者将统一只用“炭”字.

量子力学的一大成就就是证实了元素的周期性排布.按照量子力学的近似模型,原子外部的电子呈现壳层结构,满壳层的电子数为 $2n^2$, $n=1, 2, 3, 4$. 炭原子,原子序数为6,其电子构型为 $1s^2 2s^2 2p^2$, 即具有半满的壳层.一个炭原子最多可以形成4个C-C键,且键长 $\sim 1.42 \text{ \AA}$, 也就是说,炭原子之间既有多样性的成键态,又有非常强的键合,这是炭元素会表现出众多异构体(polytype, allotrope)的根本原因.已知的炭元素异构体包括石墨(graphite)、金刚石(diamond)、六角金刚石(lonsdalite)、巴基球(buckyball, 又称富勒烯, fullerene 或 buckminsterfullerene)、炭纳米管(carbon nanotube)、炭单层 gra-

phene). 成键不是很单纯的炭的存在形式还包括无定形炭(amorphous carbon)、非晶金刚石(amorphous diamond)、类金刚石(diamond-like carbon)、石墨炭(graphitic carbon)、炭晶须(whisker)、炭纤维(carbon fibers)等等. 现一一介绍如下.

1 石墨

石墨的西文为 graphite = graph (写) + ite (石头、矿) 和中文石墨对应得非常妙, 盖因石墨容易留下划痕的特性早为人类所认识的缘故, 而该词的出现应在石墨的应用之后. 石墨为片层结构, 每个炭原子在平面内有 3 个近邻, 即所谓典型的 sp^2 - 键. 两层六角格子绕垂直层面且在每层内通过一个炭原子的轴错开 30° . 石墨层内 C - C 键长 1.42\AA , 故单一炭层的杨氏模量非常大, 而层间距为 3.35\AA , 两层间靠微弱的范德瓦耳斯共价键(p - 轨道的侧向叠加) 结合, 层间容易发生滑移, 故石墨受到切向力时会解理. 铅笔就是利用石墨的这个特性. 一般大家认为石墨是黑色的, 那是因为普通石墨结晶不好的缘故. 实际上, 石墨晶体是间接带隙的固体, 其带隙为 -0.04eV , 常温下有足够数量的载流子参与导电, 和金属铋一起被称为半金属(semi-metal), 所以石墨晶体呈现典型的金属光泽(图 1). 石墨是炭的稳定结构.

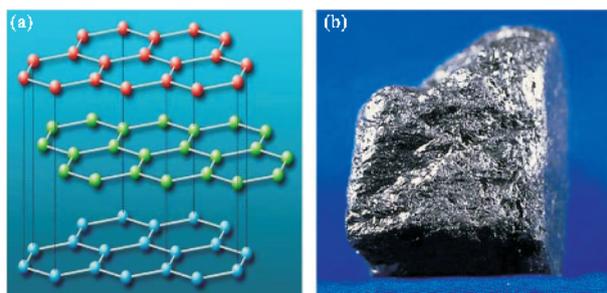


图 1 (a) 石墨的晶格结构 (b) 石墨晶体, 呈金属光泽

2 炭单层(graphene)

自从石墨的层状结构被认识以来, 人们就注意到了蜂窝状的炭单层的特殊性质. 比如, 单层石墨的杨氏模量可能是所有材料中最高的, 约为 1030GPa . 最近, graphene 的研究突然热了起来, 是因为 Novoselov 等人的一篇文章(Nature 2005 438 :197), 文中作者宣称完美 Graphene 的载流子是无质量的费米子(massless Fermion), 表现出反常的霍尔效

应. 笔者没有能力评判从一条实验拟合曲线 $E \propto k$ 得出无质量费米子(massless Fermion) 得体与否(似乎任何足够乖的函数在其零点附近针对足够小的变量变化其行为都可以近似地看作是线性的), 是否就能模仿无质量的相对论性粒子(mimic relativistic particles with zero rest mass), 只就其中文翻译罗嗦几句. 我以为将 graphene 翻译成“炭单层”较好, 理由有三 (1) graphene 本来指的物理实在就是炭单层. Novoselov 生怕这个词对物理学家们眼生, 所以赶紧解释它是炭单层(a single atomic layer of carbon, 参考文献见上). 实际上, 炭单层早就是被充分地研究了的对象(至少是从材料科学的角度). 比方说, 炭单层间夹金属的石墨会表现出许多特异性质来, 这类结构被称为 intercalation. 碱金属, 比如钾的原子加入石墨层间形成的夹心结构(intercalated structure) 和 $\text{Rb}_2\text{CsC}_{60}$ (碱金属原子在炭原子笼中) 一样, 都能表现出超导电性. Graphene, 其等价的英文表述还包括 graphite layer, graphitic layer, graphene layer, 或 graphene sheet 等. 异于“炭单层”的翻译易引起误解, 也失却了同上述几个不同表述间的等价关系. (2) 翻译成“炭单层”, 可和“炭纳米管”保持字面上的同一性, 也能照顾到两者间的渊源, 利于用相同词汇讨论炭的不同异构体. (3) 不翻译成“石墨烯”是避免由“烯”带来的“望文生义”. 一个炭单层(graphene sheet) 既不是石墨, 也和“烯”没任何关系. Graphene 被翻译成“石墨烯”, 可能是参照 Fullerene 的“富勒烯”中文译名. 不幸的是, “富勒烯”的译名同样是站不住脚的(见下)!

3 金刚石(diamond)

金刚石是炭的一种亚稳态形式, 其形成需要高温高压条件. 天然金刚石一般出现在火山口附近就是这个道理. 由于金刚石的带隙为 5.5eV , 属于宽禁带半导体, 其掺杂非常困难(到现在, n - 型掺杂还是固体物理学的难题), 所以即使是在火山熔岩中生成, 依然非常纯净. 金刚石稀有、纯净、坚硬耐磨(那是没遇到铁), 所以是高价装饰品, 为部分人所疯狂追逐. 金刚石的杨氏模量为 1.22GPa , 热导率为 $20.0\text{W cm}^{-1}\text{K}^{-1}$ (这一条可以作为金刚石的特征, 摸在手里发凉), 声速为 18000ms^{-1} , 皆为所有材料的最大值. 与杨氏模量类似但是缺乏严格定义的一个物理量是硬度, 金刚石是公认的最硬的材料, 合成比金刚石还硬的材料一直是国际材料科学界所

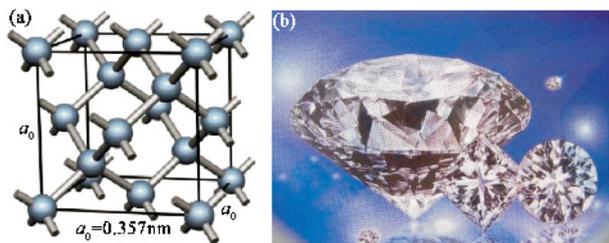


图2 (a)金刚石的晶格结构 (b)抛磨后的金刚石

追求的目标。

金刚石作为碳元素的自然形态之一要到 17 世纪才由意大利人通过实验加以确认。将金刚石在太阳光下放在凸透镜的焦点,加热到 600 °C 左右就和氧气发生反应,反应产物为 CO₂,所以可以判断金刚石的唯一成分为炭。Diamond 一词来自拉丁语 adamas(希腊语 adamant),意思是不屈服、最硬的金属的意思。我们的祖先可能见识金刚石不太早,用金刚(梵神,形象威猛、刚烈)命名是强调其硬度,当在佛教传入中国后,切削过的(好像也指成色不是顶级的)金刚石又称 Brilliant。金刚石为立方晶系,其单胞包括两套面心立方格子,其中一套格子沿另一套格子的体对角线位移 1/4 单位(图 2)。金刚石结构是由 4 个 C-C 键所支起的正四面体,即所谓的 sp³-键,形成固体的方式之一。另一种方式为图 3 所示的纤锌矿(Wurtzite)结构的金刚石,与 C-C 键上的两个碳原子相连的各三个 C-C 键呈镜面对称的构型。这样的 sp³-键固体炭较为罕见,于 1966 年才被首次发现,此后被命名为 lonsdaleite,以表彰英国著名女晶体学家 Kathleen Lonsdale (1903—1971)的学术成就。汉语就简单地称之为六角金刚石。

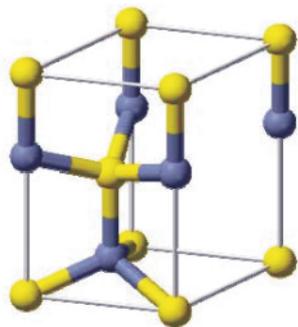


图3 炭的六角金刚石(lonsdaleite)结构

4 巴基球(Bucky ball)

由一定数量的碳原子构成的笼状(cage, clathrate)大分子,一般地用 C_n表示,其中 n 为碳原子数。

C₆₀, C₇₀, C₇₆ 和 C₈₄ 之类的笼状炭分子,存在于炭黑、油烟之类的物质中。1985 年,科学家们注意到油烟的质谱在 720 个原子质量单位的位置上存在一个特别强的峰,这才意识到这可能是炭元素一种新的存在形式,并猜测 C₆₀ 分子具有足球状的结构。C₆₀ 具有 I_h 空间群,虽然 60 个炭原子组成了 12 个五边形和 20 个六边形,但所有原子都是等价的,三个 C-C 键分成不等价的两组,一个构型为 sp^{1.236},两个为 sp^{3.236}。炭原子笼状结构的发现在国际上掀起了一阵研究热潮,作出这项发现的三位科学家 Harold W. Kroto, Richard E. Smalley 和 Robert F. Curl 获得了 1996 年度的诺贝尔化学奖。炭球结构具有很多有趣的性质,它们可以作为一个单元(motif)形成密堆积的分子晶体(图 4),在笼状结构中掺入碱金属原子,可以获得分子超导体,等等。

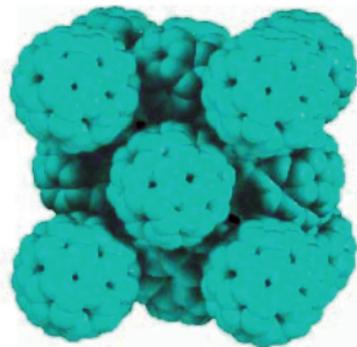


图4 C₆₀分子组成的晶体,面心立方结构,分子间靠范德瓦耳斯力结合

炭原子笼状结构的英文名字较多,包括 Bucky ball, Fullerene, Buckminster Fullerene 等,这些名字都源自美国著名的建筑师富勒(Richard Buckminster Fuller)。富勒一直倡导一种 synergy geometry(协同几何)的建筑理念,设计了三角铺排的穹顶结构(triangularly tessellated geodesic dome)(图 5)。此结构易于拆卸,所以他拿到了美国海军的一大批订单。富勒还利用三角铺排的知识于上世纪 60 年代向病毒学家解释了为什么具有 5 次对称正二十面体结构的病毒,其衣壳粒(capsomere)的数目为 12, 42, 92, ... 的问题。三角铺排与球面结晶学和准晶研究都有深刻的联系,有兴趣的读者可参阅郭可信先生的《准晶研究》一书和笔者关于球面结晶学的 PPT 讲稿。

关于炭球结构,现在文献中一般倾向于称之为 Fullerene,即以富勒的姓 Fuller,加上词尾“ene”构成。现在中文中一般将 Fullerene 译成富勒烯,笔者不敢苟同,因为它对非特别专业的人士易构成误导。

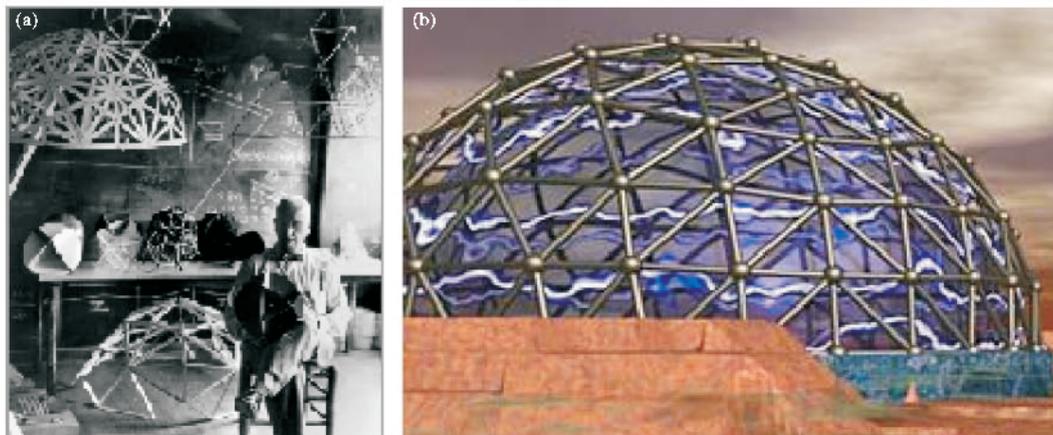


图5 (a)富勒(Richard Buckminster Fuller)美国著名建筑大师 (b)富勒倡导的测地线穹顶结构

富勒烯一词,显然是受到了乙烯(ethene,或者 ethylene)、丙烯(propene,或者 propylene)等词的启发。这些词的词尾'ene'来自希腊语 ενος(enos)。作为词尾,它仅表示该词为名词而已!汉语将 Ethene 译成乙烯,propene 译成丙烯,acetylene(ethine)译成乙炔,其中烯、炔都是近代生造的词。带'火',表示是易燃物,且略有化学知识的人们已习惯把用“烯”命名的东西归于乙烯、丙烯之类的碳氢化合物。但是,Fullerene,Graphene 和氢没有任何关系,也不易燃。如采用(富勒)炭球、炭单层的叫法,英文文献也有直接的对应词,且其中文名词也直观地给出了该炭异构体的结构形象,不带任何的曲解或强加的含义,似乎更可取些。抛此为砖,供方家讨论。

5 炭纳米管(Carbon nanotube)

很难想象一片完整的炭单层(图6)会稳定地存在。观察一下自然界里的树叶,若是相对于其大小该叶子足够薄的话,则它一定是弯折的。这是因为我们生活在一个三维世界的缘故。炭单层也会因热涨落或应力而遭破损,因而会熔化或“弯折”(“clump up”)。注意到柱面和条状二维空间是拓朴等价的,因此,将一个二维的条状晶格卷成管状应该有保存其(局域)对称性的可能,即炭管也应该是炭的可能构型。这是炭纳米管被日本科学家饭岛(Iijima)于1991年发现以后的马后炮式的思考。炭纳米管可以表现出金属型的和半导体型的导电性质,有强的力学性能和电子发射性能等优异品质,甫一出世就引起了世界范围内的研究热潮。表示炭纳米管的最简单的方式就是所谓的(n,m)标记。(n,m)决定了炭单层上的一个连接两个炭原子的矢量 $C, C = na_1 +$

ma_2 , 其中 a_1, a_2 是常规的定义炭单层晶格单胞的基矢量。想象炭管由一定宽度的炭单层卷制而成,则要求矢量 C 连接的两个炭原子在管上重合(图6)。

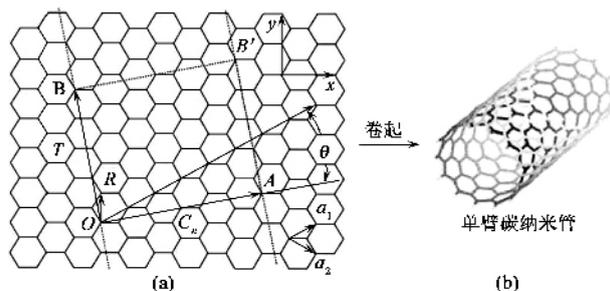


图6 在(a)图中的炭单层结构中截取矢量 C_n 为截边的一个窄条,两边对接起来,就形成了(b)图中的炭管

从上文中我们看到炭具有多种不同几何因而物理性质各异的异构体,这些众多的异构体的存在证明了 C-C 键的某种柔性,因此我们期望炭会表现出更多的灵活性来,而事实就是这样。有别于等同的 sp^2 -键, sp^3 -键或别的 sp -键,一种固体炭中各炭原子形成的几个 C-C 键,其夹角和键长可以加入一些随机的变化,从而丰富其物理性质。关于 sp -键的一般表示,请参阅本文的附加材料(见“后记”)。这样的物质包括非晶金刚石(amorphous diamond)、类金刚石炭(diamond-like carbon)、非晶石墨(amorphous carbon)、石墨炭(graphitic carbon)、高分子炭(polymeric carbon)等存在形式。当然,它们之间没有明晰的界限。

炭元素据信是宇宙中第三个出现的元素。它是生命基础性单元的骨架,为人类的存在提供必须的能量以至装饰品。金刚石不仅仅让消费者着迷,也让科学家为之着迷,就是为了研究它的比热,爱因

斯坦建立了固体量子论. 炭固体还为人类留下了许多挑战. 比如我们已知炭是熔点最高的材料, 那么它的熔点到底是多高? 如何从实验上和理论上确定炭的熔点? 这个挑战比起合成比金刚石更硬的材料也许更有实验物理和固体物理学方面的意义.

后记

(1) 关于此文中提及的炭异构体, 笔者早有讨论的打算, 然限于所知甚少, 一直未能成篇. 承复旦大学王迅院士督促, 遂向《物理》杂志匆忙交稿, 加之篇幅所限, 难免遗漏多多. 未来拟用其他形式补救.

(2) 谈到翻译, 不免提及傅雷先生. 傅雷先生为中国的文学翻译事业树立了典范, 学界有先生开创了“翻译文学”一门之说. 今年适值傅雷先生百年诞辰, 新京报 2008 年 4 月 9 日 C12 版发表了李玉民先生的纪念文章《翻译, 从原作的终点开始》, 其中谈到傅雷先生的治学精神或许对学者们翻译物理学名词有所启迪.

(3) 关于 sp - 键表示的问题, 笔者多年前写了篇英文的文章“Intermediate sp - Hybridization for Bondings in Nonplanar Covalent Molecules of Carbons”, 很幼稚, 一直未能发表. 现贴在网页 <http://surface.iphy.ac.cn/sf03/education.htm>, 供初学者参考.

· 物理新闻和动态 ·

微损伤的积累

当有几千辆并没有特别超重的卡车通过铺着沥青的公路后, 在路面上将会出现裂缝. 工程师们长期以来就观察到公路路面的破坏是由于周而复始的压力积累造成的. 早在 100 年前, 美国西北大学的 O. H. Basquin 教授就认识到, 在公路路面损伤以前, 大量重复的压力积累会加大下一次压力对路面的损害(尽管本次的压力并不很强). 他指出, 对于一个路面可承受压力的总次数是与压力的大小成幂律下降, 不同材料的路面有着不同的幂指数.

最近匈牙利德布勒森大学的 F. Kun 教授和他的同事们想从微观角度来考虑微损伤积累对材料断裂的影响和它们之间的规律. 他们将沥青看成是一种无序材料, 由许多平行的纤维组织所构成. 对于单个纤维组织的破损有两点需要考虑, 一是每个纤维组织在断裂前能承受多大的压力, 即它们的断裂阈值有多大? 二是要有多少的积累损伤就会导致单个纤维的断裂. 因为材料是在有许多小裂纹或其他微尺度的损伤存在的情况下才会发生其最终的断裂. 虽然这个材料断裂的概念早已被许多工程人员所认识, 但从来没有人将这个现象与 O. H. Basquin 教授的理论相联系, 也就是说, 没有作过定量的分析. 所以, F. Kun 教授的研究组正是从这一点出

(4) 刘寄星老师认为文中“我们的祖先可能见识金刚石不太早, 用金刚命名是强调其硬度, 当在佛教传入中国后.”一句恐怕会让人误以为我们的祖先见识金刚石在“佛教传入中国之后”. 刘老师遂后写下了一段精美的考证文字, 其治学精神之严谨, 由此可见一斑. 不敢独享, 恭录于后:

其实“金刚”二字是梵语“Vajra”之意译, 而非音译. 《三藏法数》有解曰:“金刚者, 金中最刚”, 是为证. 故完全有可能在佛教传入中国之前, 我们的祖先已见识了金刚石. 记得读过一篇关于人类认识金刚石的历史文章, 谈到过中国人认识金刚石的历史, 该文云:“在中国, 金刚石已有 3000 多年的历史. 《列子·汤问篇》:‘周穆王(公元前 1005 年—公元前 951 年)大征西戎, 献锺吾之剑, 火浣之布, 其剑长尺有咫, 炼钢赤刃, 用之切玉, 如切泥焉’. 西汉东方朔的《海内十洲记》也载有:‘周穆王时, 西胡献锺吾割玉刀及夜光常满杯, 刀长一尺, 切玉如切泥’. 不少学者认为‘锺吾剑’、‘锺吾刀’均指以金刚石为原料所制作的刀剑. 锺吾刀剑到汉、晋时已消失了. 先秦(公元前 475—221 年, 战国时期)《诗经·小雅·鹤鸣》就有‘他山之石, 可以攻玉’之说, 此‘他山之石’当然是指硬度要高于玉、可以用来切玉的石头, 其中就包括金刚石”.

此外, 据“辞源”, 金刚石亦称“切玉刀”. 中国人与玉石打交道的历史, 远在佛教传入之前千年以上. 看来, 我们的祖先见识金刚石, 可能比金刚石产地的印度人、波斯人晚些, 但恐不在佛教传入之后.

发. 他们假定对每一个纤维组织来说, 它的微损伤总和的时间变化率与压力的关系是按幂律增加. 这个假定是基于实验数据的归纳, 因为当压力增加时, 材料损伤的积累会加快. 为了简化数学模型, 他们进一步假定, 对于一个确定的压强数值, 材料的寿命也保持着一个相同的数值, 即在稳定持续的压力作用下, 当达到某个损伤阈值时, 材料就会发生断裂现象. 这样一来, 材料的寿命就直接与该时间内损伤积累的大小有关. 如果损伤积累率与压力存在着幂律关系, 则寿命也会随压力按同样的幂律指数减少. 因此匈牙利研究组认为, O. H. Basquin 教授所指出的幂指数就可直接通过测定材料的寿命或损伤积累获得. 同时通过这个断裂模型还能找到纤维组织发生灾变的特性, 当某一个纤维组织发生断裂时, 其余剩下的纤维组织将会承担更多的压力负担, 使其中一部分也迅速达到它们各自的损伤阈值而产生断裂, 从而形成如雪崩似的断裂灾变. 现在科学家们认为, 这个模型的结果如与实验紧密结合, 将会对工程设计中采用何种材料才能经久耐用有很大的帮助.

(云中客 摘自 Physical Review Letters, 7 March 2008)

Intermediate sp-Hybridization for Bonding Configurations in Nonplanar Covalent Molecules

非平面共价键分子成键构型的中间 sp-杂化

(Written in the year 2000)

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Abstract Representations for symmetric and asymmetrical intermediate sp-hybridization are provided. With given representations, the development of electronic structure in the C_{3v} -symmetrical C_2H_6 molecule and the bonding configuration in cluster C_{60} have been analyzed. The spherical structure of C_{60} does not necessarily require the fourth hybrid, h_4 , to lean along the radial direction. Rather, it runs at an angle of 3.83° from the radius in the plane bisecting a pentagon to achieve a maximum overlap with the adjacent h_4 -hybrids. By virtue of these representations, a number of properties of covalent molecules and solids can be calculated at ease.

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In the course of studying the electronic properties of covalent molecules and solids it is usually convenient to employ the concept of hybrids, i.e. some proper combinations of the atomic orbitals, which allow significant approximations to be made. A linear combination of p-orbitals with the s-orbital (termed sp-hybrid) corresponds to a directional probability distribution. With given sp-hybrids, the bond angles and a number of other relevant quantities can be calculated by simple algorithm. The most well known example of hybridization is that for carbon atoms. The carbon atom has the electronic configuration $2s^2 2p^2$ in its ground state. Generally it costs some energy to promote one s-electron to the p-orbital so as to generate the sp-hybrids, but the formation of σ -bonds of enhanced strength from these hybrids will outbalance the promotion energy. Depending on the chemical environment, either two, three or four hybrids at adjustable orientations can be formed at a carbon atom. This accounts for the rich variety of carbon-based materials.

The representations for the linear sp^1 -, planar-triangular sp^2 - and the tetrahedral sp^3 -hybridization have been worked out long ago and can be found in many textbooks devoted to bonding theory [1,2], here the atomic orbitals are either 2s- and 2p-orbitals as for carbon or 3s- and 3p-orbitals as for silicon. In terms of these hybrids the electronic structures in graphite and diamond, among many others, have been well understood [4]. However, these three simple bonding-configurations are far from enough to exhaust all possibilities for covalent structures in nature. Very often the covalent molecules exhibit a pyramidalized local geometry, which may be ascribed to an intermediate sp-hybridization, i.e. in the hybrids the p-content might be a fractional in unit of the s-content.

Two novel all-carbon structures, the spheroidal icosahedral C_{60} discovered by smalley [5] and the carbon nanotubes first synthesized by Ijima [6], have aroused the interests of researchers from a wide range of disciplines in recent years. In these macromolecules, the carbon atoms are connected at three-fold vertices to form a closed structure, where the building-blocks are pentagons, hexagons, and also minor heptagons in larger molecules [7]. To understand the electronic structure and bonding in C_{60} , Haddon made the POAV (π -orbital axis vector) analysis of C_{60} , assuming that the π -orbital makes equal angles to the three “*equivalent*” σ -bonds in nonplanar geometry, albeit actually the three σ -bonds of two distinct bond lengths subtend two different angles [8-10]. In this case, Haddon introduced the concept pyramidalization angle to quantify the nonplanarity. More surprisingly, he gave a quite reasonable plot of the pyramidalization angle as a function of the s-component in the π -bonding hybrid without referring to any explicit relation between these two quantities.

We recognized that any covalent bonding configuration at an atom, in particular those at carbon atoms, can be well described with proper sp-hybridization. From the viewpoint of mathematics, the four hybrids are linear transformation of one s- and three p-orbitals realized through a 4×4 matrix. The orthonormality requirement upon the resulting hybrids in conjunction with the possible symmetry of the bonds they form may considerably reduce the number of independent variables in the transformation. The principle of orthogonality is not a physical requirement but it exists to ensure a physically transparent breakdown of the total valence electronic charge of a molecule into separate contributions, one from each hybrid. Taking the C_{60} molecule for instance, the two distinct angles subtended by three σ -bonds can uniquely determine the compositions of the hybrids, hence the orientation of the fourth hybrid. Therefore,

it is absolute unnecessary, and also improper, to adopt the unjustified assumption that the “ π -orbital” leans along the radial direction with a nodal at the cage surface of C_{60} [11]. In this article, we will give an explicit, general representation of the intermediate sp -hybrids for two cases: (a) three equivalent σ -bonding hybrids, the fourth hybrid h_4 can form either a π -like bond or a σ -bond with other h_4 at adjacent atoms. This is the case when the bonds exhibit C_{3v} symmetry. Here we use the phrase “ π -like bond” since the bonding between two h_4 -hybrids is no more of pure π -nature. (b) Only two among the three σ -bonding hybrids are equivalent as in C_{60} . In the latter case the local geometry is characterized by four bond angles. A few properties of the carbon macromolecules can be discussed by virtue of this representation.

We first consider the simpler case when three of the four intermediate sp -hybrids, denoted as $sp^{2+\delta}$ -hybrids, are equivalent. To start with, let us write down a representation for the sp^2 -hybridization in the form

$$\begin{aligned}
 h_1 &= (3)^{-1/2}(s + \sqrt{1/2}p_x + \sqrt{3/2}p_y) \\
 h_2 &= (3)^{-1/2}(s + \sqrt{1/2}p_x - \sqrt{3/2}p_y) \\
 h_3 &= (3)^{-1/2}(s - \sqrt{2}p_x) \\
 h_4 &= p_z
 \end{aligned} \tag{1}$$

One can verify with a pencil that the hybrids in (1) are indeed orthonormal and the sp -ratio in the first three hybrids is 1:2. In order to construct the symmetrical $sp^{2+\delta}$ -hybrids, an equal part of p_z should be admixed into the first three hybrids in (1) to elevate the p -content. Correspondingly, some s -component will be incorporated into h_4 to make it an $s^{\delta/3}p$ -hybrid as required by the orthogonality condition. After a proper adjustment of other coefficients, a correct representation for the $sp^{2+\delta}$ -hybridization is immediately achieved,

$$\begin{aligned}
h_1 &= (3+\delta)^{-1/2}(s + \sqrt{(3+\delta)/6}p_x + \sqrt{(3+\delta)/2}p_y - \sqrt{\delta/3}p_z) \\
h_2 &= (3+\delta)^{-1/2}(s + \sqrt{(3+\delta)/6}p_x - \sqrt{(3+\delta)/2}p_y - \sqrt{\delta/3}p_z) \\
h_3 &= (3+\delta)^{-1/2}(s - \sqrt{(6+2\delta)/3}p_x - \sqrt{\delta/3}p_z) \\
h_4 &= (3+\delta)^{-1/2}(\sqrt{\delta}s + \sqrt{3}p_z)
\end{aligned} \tag{2}$$

It degenerates into the customary representation for sp^2 -hybridization in (1) at $\delta=0$, and at $\delta=1$ it turns into

$$\begin{aligned}
h_1 &= 1/2(s + \sqrt{2/3}p_x + \sqrt{2}p_y - p_z/\sqrt{3}) \\
h_2 &= 1/2(s + \sqrt{2/3}p_x - \sqrt{2}p_y - p_z/\sqrt{3}) \\
h_3 &= 1/2(s - \sqrt{2/3}p_x - p_z/\sqrt{3}) \\
h_4 &= 1/2(s + \sqrt{3}p_z)
\end{aligned} \tag{3}$$

a representation for the sp^3 – hybridization other than the conventional form

$$\begin{aligned}
h_1 &= 1/2(s + p_x + p_y + p_z) \\
h_2 &= 1/2(s + p_x - p_y - p_z) \\
h_3 &= 1/2(s - p_x + p_y - p_z) \\
h_4 &= 1/2(s - p_x - p_y + p_z)
\end{aligned} \tag{4}$$

The transformation (2) contains a unique parameter δ . The orientation of the four hybrids can be characterized with two bond angles, θ subtended by any pair of h_1 , h_2 and h_3 , and ϕ that h_4 runs to any of the other three hybrids (Fig.1a). They are simple functions of the parameter δ ,

$$\cos(\theta) = -\sqrt{\delta/(6+3\delta)} \tag{5.1}$$

and

$$\cos(\phi) = -1/(2+\delta). \tag{5.2}$$

Clearly, either θ or ϕ suffices to define the local geometry of the symmetrical $sp^{2+\delta}$ – bonded structures. When δ increases from zero to unity, both angles, starting from 90°

and 120° respectively, approach simultaneously a value of 109.47° (Fig.1b), the bonding configuration found in the tetrahedral structure.

Note that the parameter δ is not limited to unity as deeply rooted in our belief. Let us analyze, for instance, the hybrids at carbon atom in the ethane molecule C_2H_6 which displays C_{3v} symmetry. The experimental value of the angle $\angle CCH$ is 111.17° [12], therefore, from the knowledge of solid geometry, an angle $\angle HCH = 107.72^\circ$ is expected. We anticipate the four σ -bonding hybrids of the carbon atom in C_2H_6 be given by representation (2). To prove this, substituting $\theta = 111.17^\circ$ into (5.1) and solving for δ , one obtains $\delta = 1.2845$. Thus, one finds that the atomic orbitals on the carbon atom is $sp^{3.28}$ -hybridized to form the C-H bonds in C_2H_6 . This value of δ , from (5.2), gives rise to an angle of exactly 107.72° between two neighboring C-H bonds. That's to say that both the homopolar and heteropolar bonds formed by hybrids at carbon atoms have a maximum probability along the intra-atomic connections.

As confirmed by the analysis above, the hybrids h_1, h_2 and h_3 for the C-H bonds have the composition $sp^{3.28}$, and h_4 for the C-C bond is an $s^{0.428}p$ -hybrid. With these given hybrids, the development of the electronic structure in C_2H_6 can be traced following the scheme in Harrison [3,4] (Fig.2). The covalent energy of the C-C bond in C_2H_6 is

$$E_{CC}^{cov} = -(-3V_{pp\sigma} + 2\sqrt{3\delta}V_{sp\sigma} + \delta V_{ss\sigma}) / (3 + \delta). \quad (6)$$

The values of the hopping integrals $V_{pp\sigma}$, $V_{sp\sigma}$ and $V_{ss\sigma}$ can be derived from the universal formula (1-21) in Harrison [4]. For a C-C bond of 0.1535nm in length, $E_{CC}^{cov} = -10.60\text{eV}$. Correspondingly, the covalent energy of the C-H bond E_{CH}^{cov} is

-11.97eV . We then proceed to write the molecular state in combination of the resulting bonding or antibonding orbitals

$$|\text{MO}\rangle = u_0|\psi_{\text{C-C}}\rangle + \sum_{i=1}^6 u_i|\psi_{\text{C-H},i}\rangle \quad (7)$$

The energy levels of the molecular state can be determined by minimizing the energy of this molecular state with respect to the coefficients and diagonalizing the resulting 7×7 Hamiltonian matrix [4]. The coupling between the bonds can be reasonably approximated by that between the hybrids at carbon atoms. Denote the coupling between h_1 and h_2 as α , and that between h_4 and h_1 as β , then the eigenvalues of the Hamiltonian are given by

$$\begin{aligned} \lambda_{1,2} &= \varepsilon_2 + (\varepsilon_1 - u_2 + 2\alpha)/2 \pm \sqrt{(\varepsilon_1 - \varepsilon_2 - 2\alpha)^2/4 + 6\beta^2} \\ \lambda_{3,4,5,6} &= \varepsilon_2 - \alpha \\ \lambda_7 &= \varepsilon_2 + 2\alpha \end{aligned} \quad (8)$$

where ε_1 and ε_2 are the term values of the C-C bond and the C-H bond, respectively. The coupling constants α and β can be directly calculated from (2), $\alpha = -1.94\text{eV}$, and $\beta = -2.17\text{eV}$. The C_2H_6 molecule has just 14 electrons to occupy the 7 bonding molecular orbitals (Fig.2).

Now we turn to the case when only two of the hybrids form equivalent σ -bonds as found in some fullerene molecules and carbon nanotubes. We carry out the case study of the C_{60} molecule in which the two σ -bonds in connection to one pentagon and one hexagon, denoted as b_{hp} , are equivalent while the third one that separates two hexagons, denoted as b_{hh} , differs both in orientation and bond length. To signify this asymmetry, an extra parameter should be introduced into the representation (2). By constructing the proper asymmetrical hybrids, the following

considerations might be conducive: (1) without any loss of generality, the hybrid h_4 is supposed to contain only contributions from s- and p_z -orbitals; (2) h_2 and h_3 are made equivalent, i.e. subtending identical angles to the other two hybrids. Bearing these in mind, the following presentation can be readily obtained,

$$\begin{pmatrix} h1 \\ h2 \\ h3 \\ h4 \end{pmatrix} = \begin{pmatrix} \sqrt{a-2\gamma a} & \sqrt{\gamma} & -\sqrt{\gamma} & -\sqrt{(1-a)(1-2\gamma)} \\ \sqrt{\gamma a} & (1-\sqrt{1-2\gamma})/2 & (1+\sqrt{1-2\gamma})/2 & -\sqrt{\gamma(1-a)} \\ \sqrt{\gamma a} & -(1+\sqrt{1-2\gamma})/2 & (-1+\sqrt{1-2\gamma})/2 & -\sqrt{\gamma(1-a)} \\ \sqrt{1-a} & 0 & 0 & \sqrt{a} \end{pmatrix} \begin{pmatrix} s \\ p_x \\ p_y \\ p_z \end{pmatrix} \quad (9)$$

The role of the parameters a and γ is to be understood in this manner. While a denotes the proportion of p_z -component in the h_4 -hybrid, γ signifies the apportioning of the remaining p_z -component among the other three hybrids. As expected, this representation reproduces the sp^3 - hybridization at $a=3/4$, $\gamma=1/3$ (another linear transformation of the representation (4)) and the sp^2 - hybridization at $a=1$, $\gamma=1/3$. The geometry of these hybrids make is characterized by four angles, θ_{41} , $\theta_{42} = \theta_{43}$, ϕ_{23} and $\phi_{12} = \phi_{13}$, but only two of them are independent. They are explicit functions of a and γ

$$\cos \theta_{41} = -\sqrt{(1-a)(1-2\gamma)/(1-a+2\gamma a)} \quad (10.1)$$

$$\cos \theta_{42} = -\sqrt{\gamma(1-a)/(1-\gamma a)} \quad (10.2)$$

$$\cos \phi_{12} = -\sqrt{\gamma a^2(1-2\gamma)/(1-\gamma a)(1-a+2\gamma a)} \quad (10.3)$$

$$\cos \phi_{23} = -\gamma a/(1-\gamma a). \quad (10.4)$$

Representation (9) and the relations (10.1-10.4) can be applied to analyze the macromolecule C_{60} . At any carbon atom in C_{60} , $\phi_{12} = \phi_{13} = 120^\circ$ and $\phi_{23} = 108^\circ$ (Fig.3). If, as experimentally determined, that $b_{hh} = 0.141\text{nm}$ and $b_{hp} = 0.145\text{nm}$, then the spherical shell enclosing the C_{60} molecule should have a diameter of 0.691nm , rather

than 0.7 nm [11] or 0.71 nm [13]. Consequently, the radial through a vortex runs at an angle of 101.67° to the bond in connection to two hexagons and of 101.62° to the bonds separating the hexagon from a pentagon. These two angles show only negligible difference, confirming the nearly spherical conformation of this macromolecule. Many questions can be raised about the bonding configuration in this structure: what for an sp -hybridization leads to such a geometry, does the fourth orbital, as it has been treated, lie along the radial direction making equal angles with the three σ -bonding hybrids, and so on.

To answer these questions, let us first find the hybrids that give the correct bond orientations. Since $\phi_{12} = \phi_{13} = 120^\circ$ and $\phi_{23} = 108^\circ$, by solving equations (10.3) and (10.4) the parameters a and γ are determined, $a = 0.91934$, $\gamma = 0.25677$. Thus the angles θ_{41} and θ_{42} , from (10.1) and (10.2), are accordingly 105.45° and 91.55° , respectively. We see that, in order to adopt the cage geometry, the three σ -bonding hybrids at a carbon atom in C_{60} might contain a small portion of p_z , namely 3.92% in h_1 and 2.07% in h_2 and h_3 . Therefore, the sp -mixing in h_1 is 1:1.236, and in h_2 as well as in h_3 it is 1:3.236. The fourth hybrid is nearly a pure p -orbit, yet mixed with about 8.1% s -content. From relation (10.1-10.2) one sees that h_4 does not point along the radial direction, but rather makes an angle of $\approx 3.83^\circ$ to the radial direction in the plane bisecting the pentagon attached to that carbon atom. This indeed leads to an enhanced overlap between h_4 -hybrids at adjacent carbon atoms, as confirmed by the following simple calculation. The covalent energy of two coplanar h_4 -hybrids at the angle of 2θ is given by

$$-E_c = (1-a)V_{ss\sigma} + 2\sqrt{a(1-a)}\sin\theta V_{sp\sigma} + a(\cos^2\theta V_{pp\pi} - \sin^2\theta V_{pp\sigma}) \quad (11)$$

In comparison to the situation when h_4 lies along the radial direction, the covalent energy of the actual “ π -like” bond separated by b_{hh} is 0.08eV larger, and that at a distance of b_{hp} increases for 0.13eV.

In summary, explicit representations for the symmetrical and asymmetrical intermediate $sp^{2+\delta}$ hybridization are formulated, and they have also been applied to the quantitative discussion of the electronic structure evolution in C_2H_6 and the bonding configuration in C_{60} . It was shown that the C_{60} molecule strives for a cage geometry by bending the σ -bonds, yet this does not necessarily require the fourth hybrid, of only 8% s-character, to be directed radially. With given representation, the calculation of valence configuration and of many other quantities referring to a specific molecular geometry is significantly facilitated. It also enables us to make very elementary but reasonably quantitative discussions of a number of properties. Remarkably, the continuous variation of the parameter a and γ across the critical points $a=3/4, \gamma=1/3$ and $a=1, \gamma=1/3$ may describe the situation when the symmetry is broken. This is especially useful for the process of rehybridization, as by evaluating the shear constants relating to the reduction of local symmetry, for instance, C_{44} in a zincblende structure.

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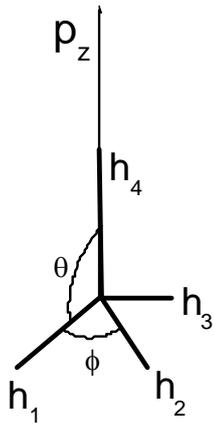
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Figure Captions

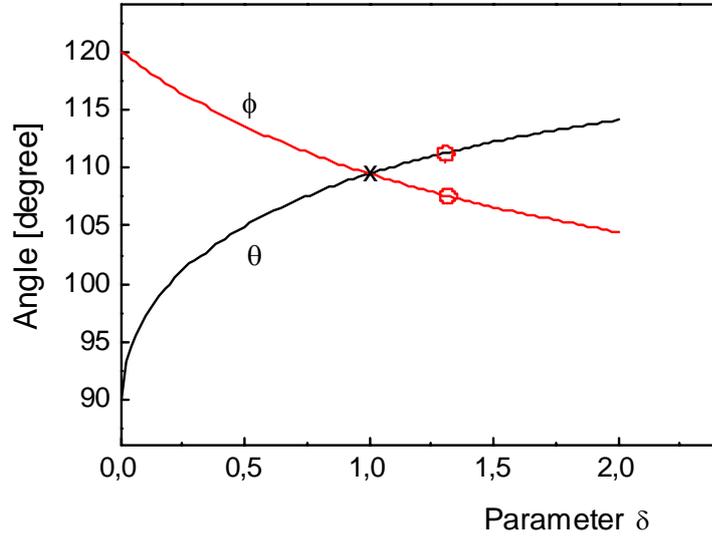
Fig.1. (a) Illustrative diagram of the hybrids for the construction of C_{3v} symmetrical bonds; (b) Variation of the angles θ and ϕ characterizing a C_{3v} local bonding with the parameter δ . The cross corresponds to the sp^3 -hybridization in diamond while the circles correspond to the situation in C_2H_6 .

Fig.2. Development of the electronic structure of C_2H_6 . The C 2s- and 2p-states are transformed into four hybridized states. The h_4 -hybrid is combined with h_4 on the other carbon atom to form the C-C bond while the h_1 through h_3 -hybrids are combined with H 1s-state. The coupling between the bonds has split the two bonding and two anti-bonding orbitals each into four. The numbers in brackets denote the degeneracy of the energy levels drawn in bold line.

Figure 3. (a) The structure of the C_{60} molecule and (b) the orientation of hybrids at a carbon atom.



(a)



(b)

Figure 1

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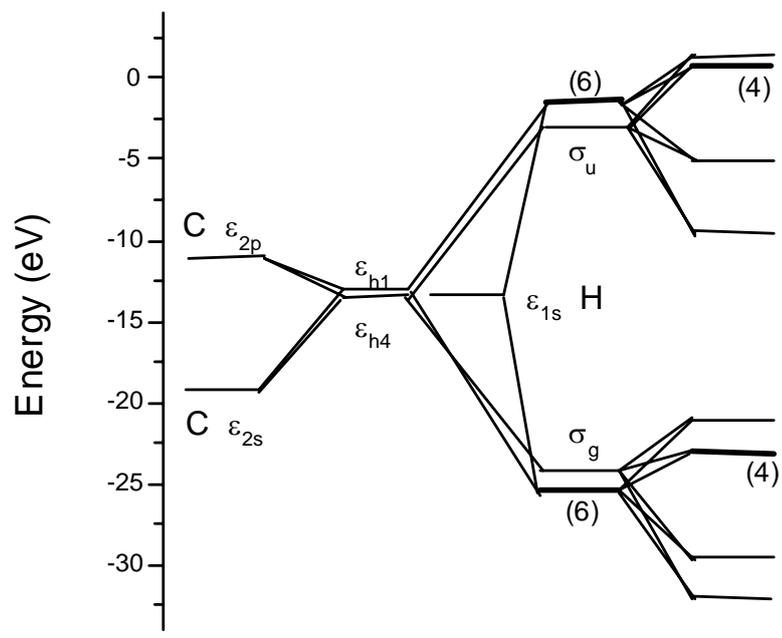
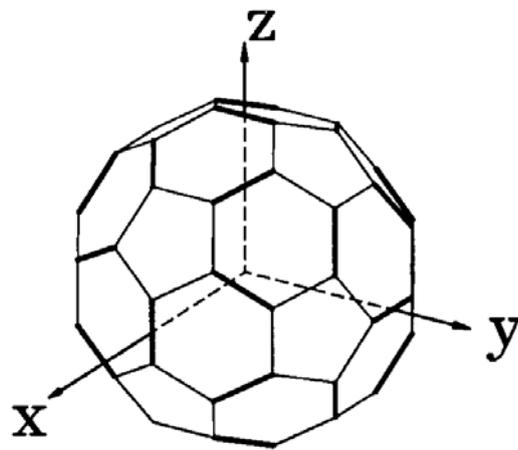
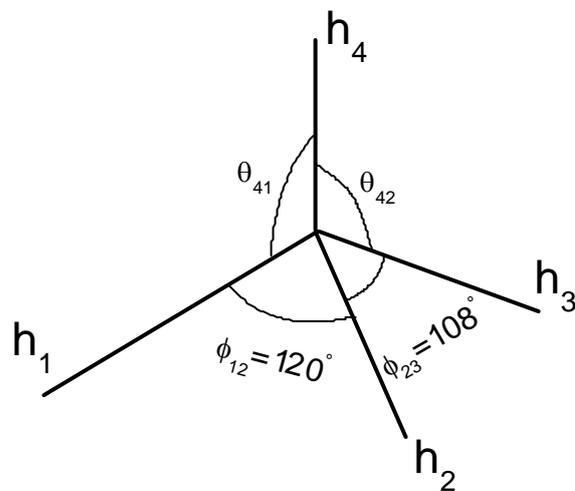


Figure .2

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(a)



(b)

Figure 3

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