生物过程中的量子效应和仿生量子器件

孙昌璞

中国科学院理论物理研究所

http://power.itp.ac.cn/~suncp/quantum.htm

The Chinese Academy of Science

报告内容

1. 生命世界的量子现象

2. 鸟迁徙的量子指南针
   - 自旋纠缠态化学
   - 磁场的超灵敏识别与量子相变

3. 光合作用的量子效应
   - 二维光子回波光谱
   - 光合仿生量子器件

生命是什么？　一个物理学家的观点和影响

***What is Life ?*, Cambridge, 1946.**

Erwin Schrödinger
1887-1961

中心法则：
“就基因分子的图式来说，微型密码是丝毫不错地对应于一个高度复杂的特定的发育计划，并且包含了使密码发生作用的手段，这一点已经不再是难以想象的了。”

生命就是不停从外界获取能量来维持自身的有序，防止熵值的增大

DNA双螺旋结构的发现

１９５３年４，沃森与克里克提出了ＤＮＡ的结构和自我复制机制。这篇论文被普遍视作分子生物学时代的开端。富兰克林和威尔金斯通过Ｘ射线衍射获得的ＤＮＡ晶体结构照片。沃森、克里克和威尔金斯共同获得１９６２年的诺贝尔奖。

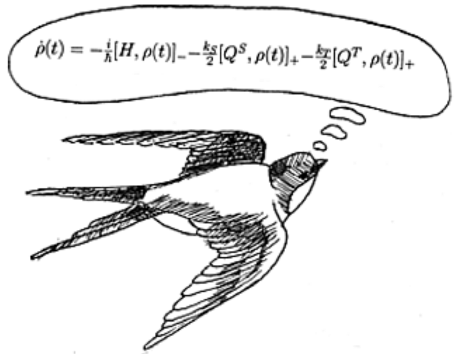
ITP
The Chinese Academy of Science

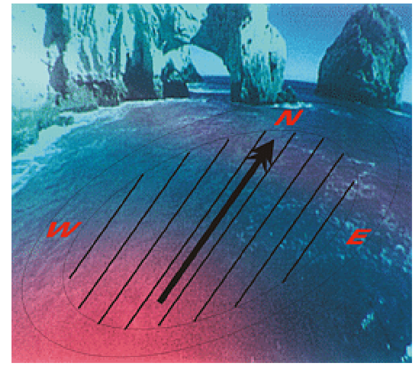
自由基(free radical pair)机制：自旋化学

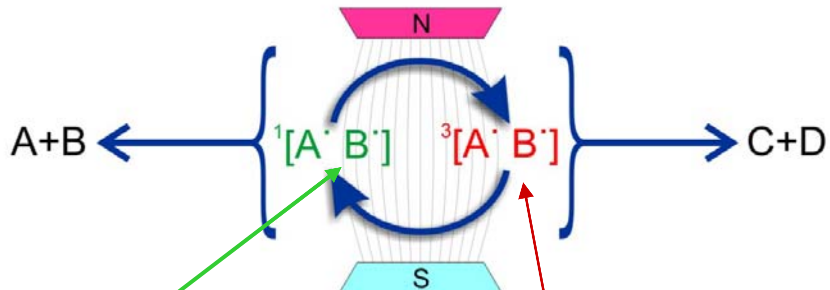
Biophysical Journal Volume 78 February 2000 707–718

A Model for Photoreceptor-Based Magnetoreception in Birds

Thorsten Ritz, Salih Adem, and Klaus Schulten



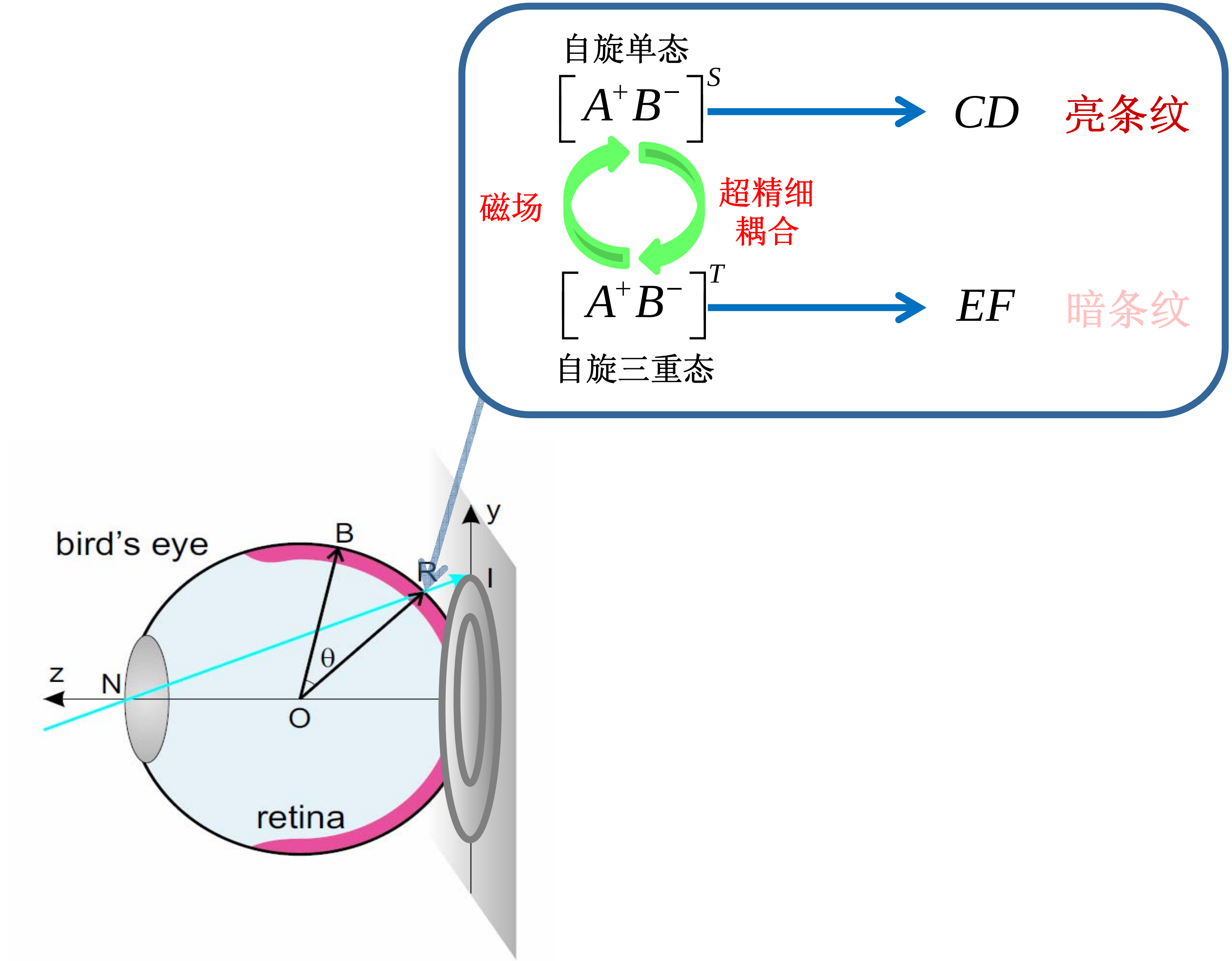




$$|0,0\rangle = (\uparrow\downarrow - \downarrow\uparrow)/\sqrt{2} \Big\} \quad s = 0 \quad \text{(singlet)}$$

$$\left.\begin{aligned} |1,1\rangle &= \uparrow\uparrow \\ |1,0\rangle &= (\uparrow\downarrow + \downarrow\uparrow)/\sqrt{2} \\ |1,-1\rangle &= \downarrow\downarrow \end{aligned}\right\} \quad s = 1 \quad \text{(triplet)}$$

鸟类眼睛感受地磁场原理



Chemical compass model of avian magnetoreception

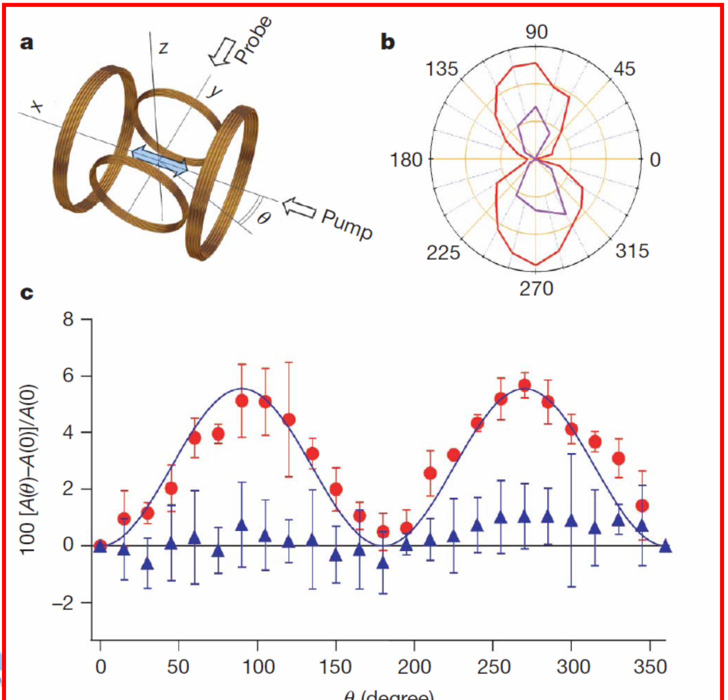
Kiminori Maeda[1]*, Kevin B. Henbest[1]*, Filippo Cintolesi[2], Ilya Kuprov[2], Christopher T. Rodgers[2], Paul A. Liddell[3], Devens Gust[3], Christiane R. Timmel[1] & P. J. Hore[2]

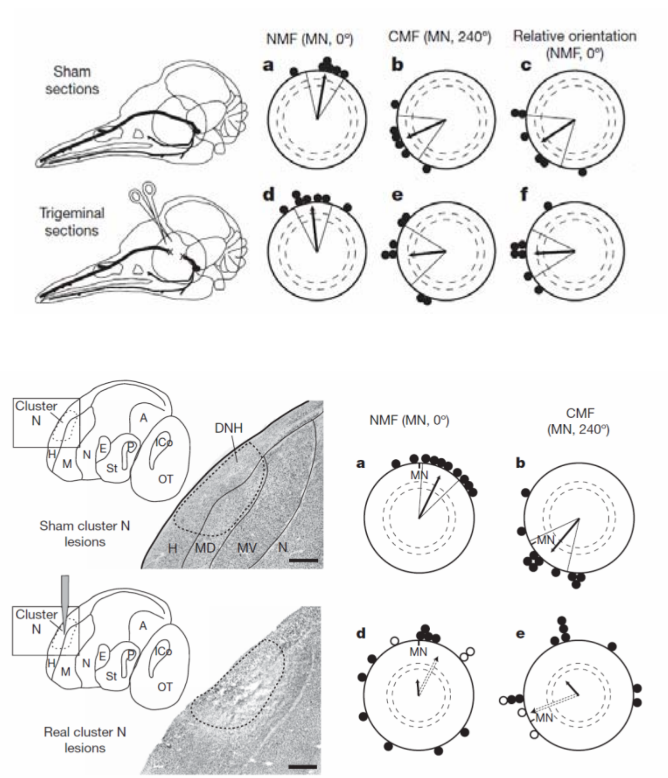
Nature, Vol 453| 15 May 2008

Visual but not trigeminal mediation of magnetic compass information in a migratory bird

Manuela Zapka[1], Dominik Heyers[1], Christine M. Hein[1], Svenja Engels[1], Nils-Lasse Schneider[1], Jörg Hans[1], Simon Weiler[1], David Dreyer[1], Dmitry Kishkinev[1], J. Martin Wild[2] & Henrik Mouritsen[1]

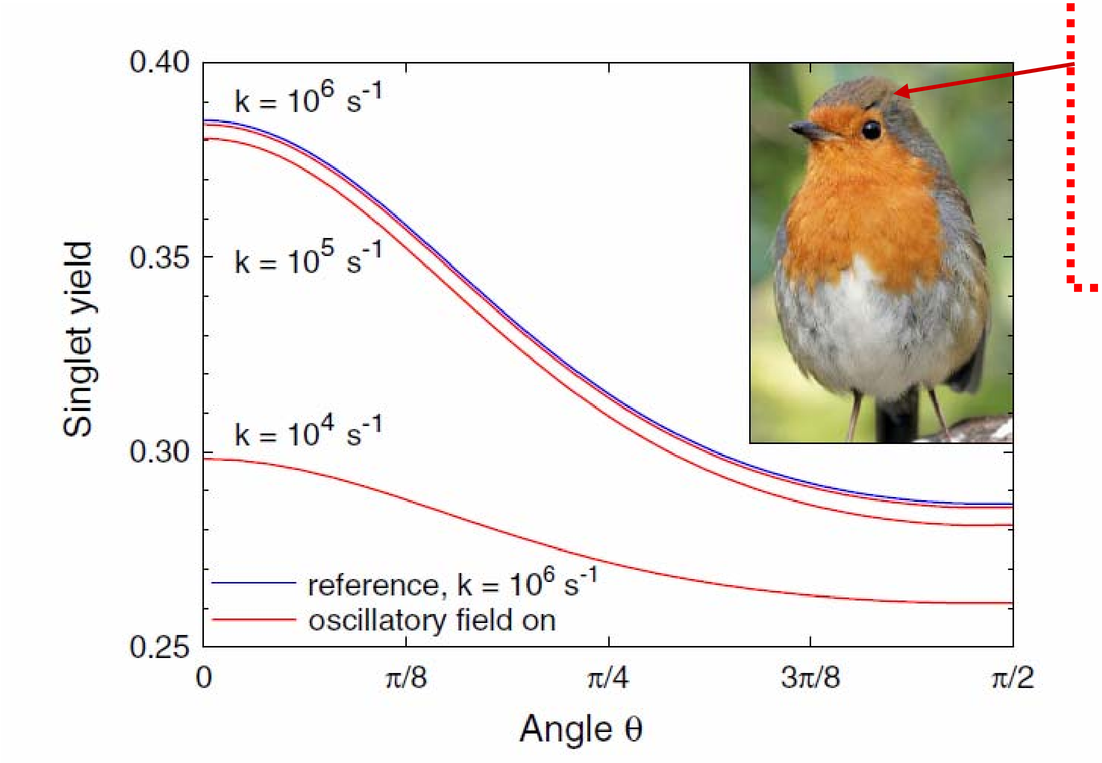
Nature ,Vol 461|29 October 2009

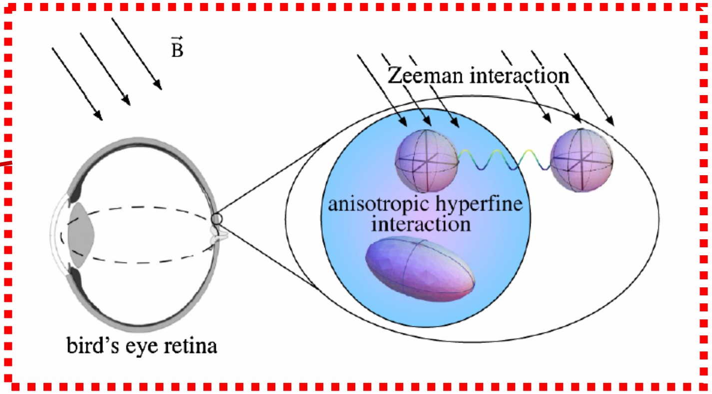


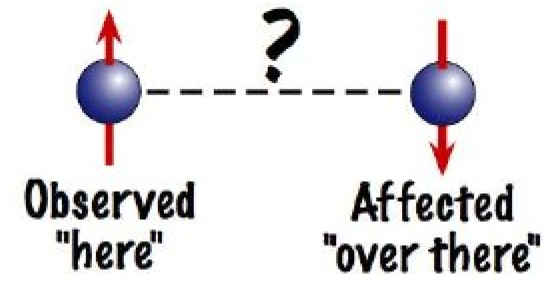


量子纠缠的作用

Guager et al , Phys. Rev. Lett. 106, 040503 (2011)







弱磁强计探测：“临界”系统的动力学敏感性

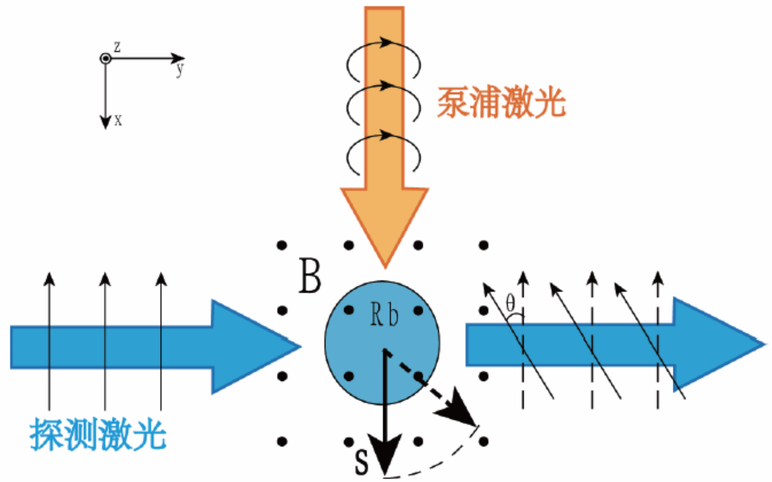


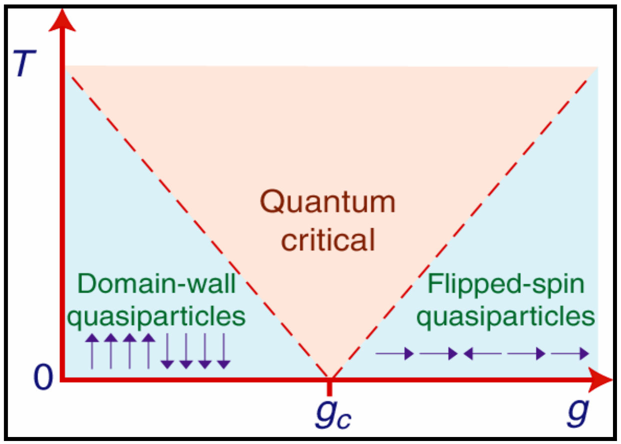
图 1. 原子磁强计原理示意图。

超高灵敏度的冷原子磁强计

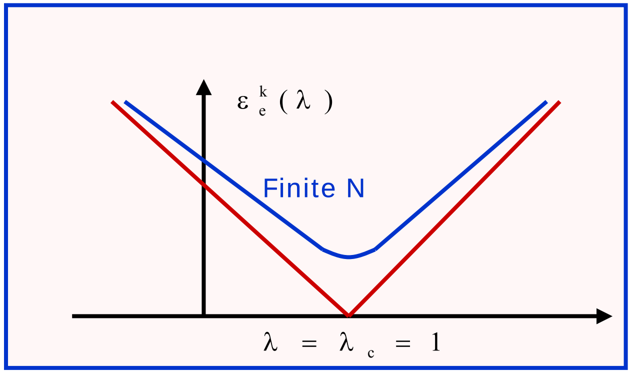
美国普林斯顿大学**Romalis** 小组**2002** 年研发的原子磁强计，灵敏度为**10 fT / √Hz**，理论上可达**2aT/ √Hz**，比超导 **SQUID** 磁强计灵敏度高三个数量级

ITP
The Chinese Academy of Science

强关联固态系统的参数操纵引起量子相变



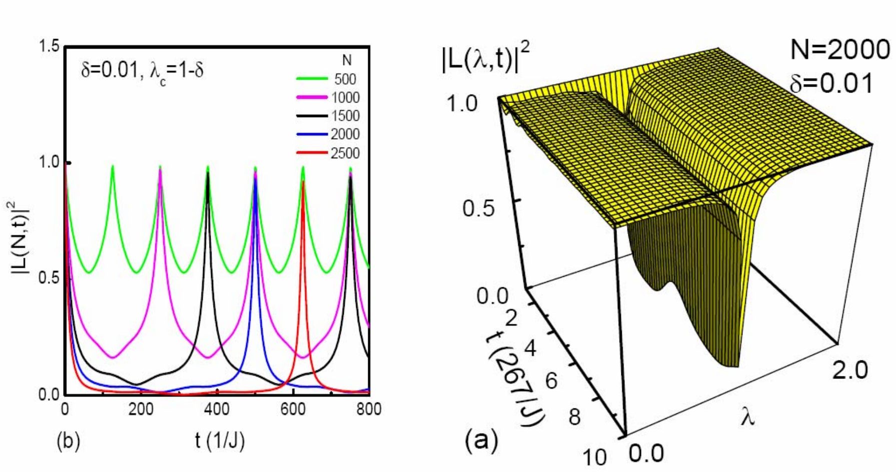
S Sachdev, (2000),
Quantum Phase Transitions.
Cambridge University Press



$$\varepsilon_e^k(\lambda) = 2J\sqrt{1+\lambda^2 - 2\lambda\cos(ka)}$$

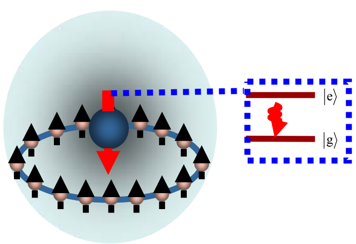
Quan, Song, Liu, Zanardi, Sun, Phys. Rev. Lett. 96, 140604 (2006)

我们的理论预言与德国Suter小组的实验证实

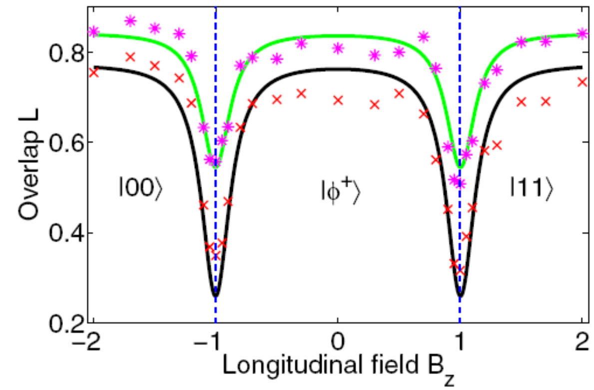


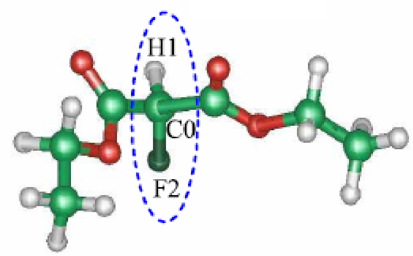
Critical Point

Loschmidt Echo



PRL 100, 100501 (2008)





环境诱导量子退相干及其量子相变的增强作用

Quan et al , Phys. Rev. Lett. 96, 140604 (2006)-引文[6]

2006年， 我们研究了单个量子比特与临界环境的相互作用，发现了量子相变导致退相干增强的量子混沌效应。由于联系了凝聚态物理中的量子相变、非平衡统计物理中的量子混沌和量子信息中的量子退相干，得到不同领域科学家的重视，引发一系列后续的工作。目前引用已经超过**160**次，得到德国、加拿大、意大利和中国的**4**个实验的证实。该工作获国家自然科学**2**等奖和全国优秀博士论文

加拿大 Laflamme 小组实验

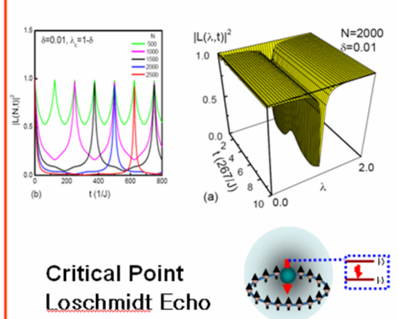
Phys.Rev. A 79,012305 (2009)

引文中强调该工作方向性的贡献

There has been a recent flurry of activity following the observation [6] that the proximity to a quantum critical point enhances the sensitivity of a system to external perturbations, as measured by quantum-information-theoretical quantities such as the Loschmidt echo [6] or the ground-state fidelity [7]. Exploiting such sensitivity, one can detect quantum criticality by coupling an additional spin as a probe to the system undergoing a QPT. This was suggested in [8] and demonstrated in [9], where the local coupling to the probe qubit was used as the perturbation.

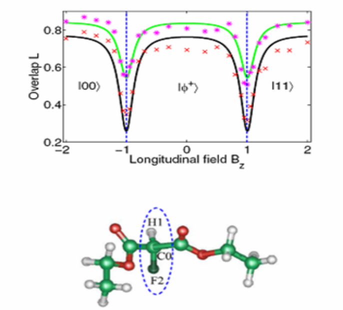
我们的理论

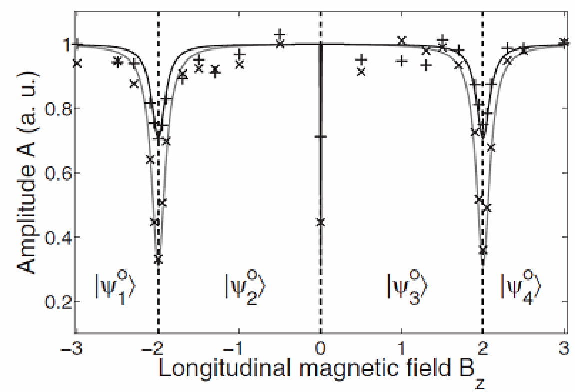
Quan et al , PRL , 96, (2006)



德国Suter小组的实验证实

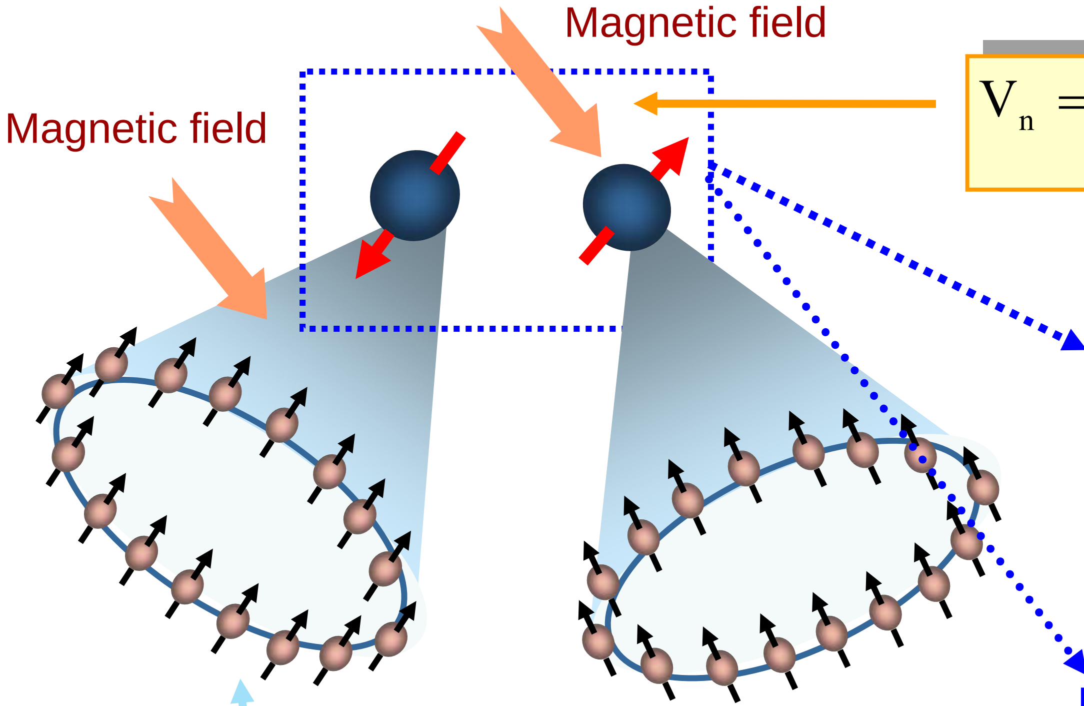
PRL 100, 100501 (2008)





ITP
The Chinese Academy of Science

量子相变辅助的弱磁场探测



$$V_n = \varepsilon\sigma_n^z + \Delta\sigma_n^x + Jg\sigma_n^x \sum_j I_{n,j}^x,$$

$$|S\rangle_e = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle_e - |\downarrow\uparrow\rangle_e)$$

自旋单态

磁场

超精细耦合

$$|T_+\rangle_e = |\uparrow\uparrow\rangle_e,\ |T_-\rangle_e = |\downarrow\downarrow\rangle_e$$

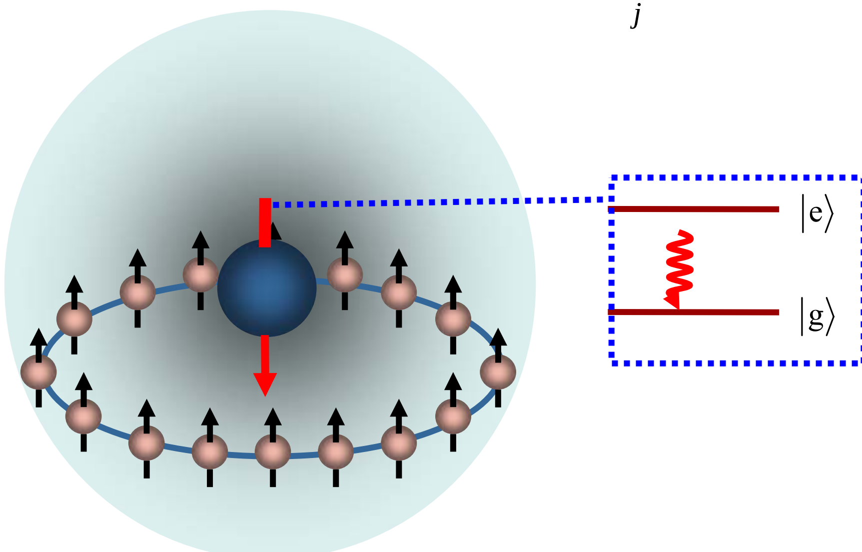
$$|T_0\rangle_e = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle_e + |\downarrow\uparrow\rangle_e)$$

自旋三重态

$$H_n = J\sum_{j=1}^{N}(I_{n,j}^z I_{n,j+1}^z + \lambda I_{n,j}^x)$$

推广的Hepp-Coleman模型描述量子测量

$$H = H_0 + H_1 = -J\sum_j (\sigma_j^z \sigma_{j+1}^z + g\sigma_j^x + \delta|e\rangle\langle e|\sigma_j^x)$$



$$\mathrm{H_e} = \mathrm{H_e}(\lambda) = \mathrm{H_g} + \mathrm{V_e}$$

$$V_e = -J\delta\sum_j \sigma_j^x$$

$$H_g = H_0 = -J\sum_j (\sigma_j^z \sigma_{j+1}^z + g\sigma_j^x)$$

$$|\psi(0)\rangle = (c_g|g\rangle + c_e|e\rangle)\otimes|G\rangle_g \longrightarrow |\psi(t)\rangle = c_g|g\rangle\otimes|\varphi_g(t)\rangle + c_e|e\rangle\otimes|\varphi_e(t)\rangle$$

$$\rho_S(t) = c_g c_g^*|g\rangle\langle g| + c_e c_e^*|e\rangle\langle e| + \boxed{\langle\phi_e|\phi_g\rangle} c_g c_e^*|g\rangle\langle e| + \langle\phi_g|\phi_e\rangle c_e c_g^*|e\rangle\langle g|$$

退相干因子

退相干因子和Loschmidt echo

约化密度矩阵 $$\boxed{[\rho_s(t)]_{eg} = c_g c_e^* D(t)}$$

$$D(t) = \langle \varphi_g(t) | \varphi_e(t) \rangle \qquad |\varphi_\alpha(t)\rangle = \exp(-iH_\alpha t)|G\rangle_g$$

退相干因子(Loschmidt echo)

$$\boxed{L(\lambda,t) = \left|\left\langle \phi_g(t) | \phi_e(t) \right\rangle\right|^2 = \left|\left\langle G\right|_g \exp(iH_g t)\exp(-iH_e t)\left|G\right\rangle_g\right|^2}$$

$$L(\lambda,t) = \prod_{k>0}[1 - \sin^2(2\alpha_k)\sin^2(\varepsilon_e^k t)].$$

ITP
The Chinese Academy of Science

基态变换

$$H_e = -J\sum_j [\sigma_j^z \sigma_{j+1}^z + (g+\delta)\sigma_j^x] = \sum_k \varepsilon_e^k (A_k^\dagger A_k - 1/2)$$

$$H_g = -J\sum_j (\sigma_j^z \sigma_{j+1}^z + g\sigma_j^x) = \sum_k \varepsilon_g^k (B_k^\dagger B_k - 1/2)$$

$$\mathrm{A_k}|\mathrm{G}\rangle_\mathrm{e} = 0 \qquad \mathrm{B_k}|\mathrm{G}\rangle_\mathrm{g} = 0$$

$$\mathrm{B_{\pm k}} = \cos(\alpha_\mathrm{k})\mathrm{A_{\pm k}} - i\sin(\alpha_\mathrm{k})(\mathrm{A_{\mp k}})^\dagger,$$

BCS-like ground state:

$$|\mathrm{G}\rangle_\mathrm{g} = \prod_{\mathrm{k}>0}\left[i\cos(\alpha_\mathrm{k}) + \sin(\alpha_\mathrm{k})\mathrm{A_k^\dagger A_{-k}^\dagger}\right]|\mathrm{G}\rangle_\mathrm{e}$$

H. T. Quan, Z. Song, X. F. Liu, and C. P. Sun, PRL 96, 140604 (2006)

Born-Oppenheimer近似

快变本征态

$$E \simeq B + Jg\cos\theta \sum_{j=1}^{N} I_j^x,$$

$$|+\rangle \simeq \cos\theta'|\uparrow\rangle + \sin\theta'|\downarrow\rangle,$$

$$|-\rangle \simeq \sin\theta'|\uparrow\rangle - \cos\theta'|\downarrow\rangle,$$

$$\theta' = \frac{\pi}{4} - \frac{\theta}{2}.$$

$$H_n^{\pm} = J\sum_{j=1}^{N}\left[I_{n,j}^z I_{n,j+1}^z + \lambda_{\pm}(\theta) I_{n,j}^x\right]$$

单态化学反应产物 和 Loschmidt Echo (I)

时间演化

$$\chi(0) = |S\rangle \otimes \chi_a \otimes \chi_2$$

$$\rho_S(t) = \frac{1}{2}\left[|+-\rangle\langle+-| + |-+\rangle\langle-+| - D(t)|+-\rangle\langle-+| - D^*(t)|-+\rangle\langle+-|\right]$$

Loschmidt Echo

$$L(t) = D(t) = \mathrm{tr}\left|U \chi U\right|^{2}$$

单态反应产物

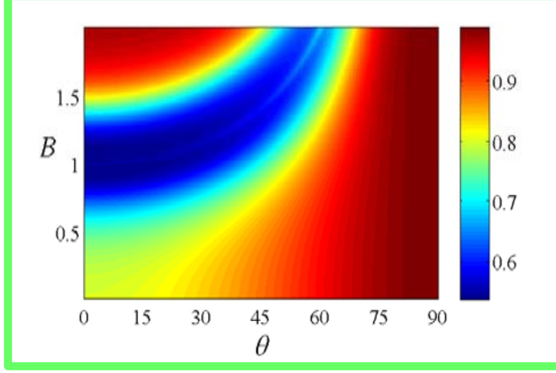
$$P_S(t) = \int_0^t r_c(t') f_S(t') dt',$$

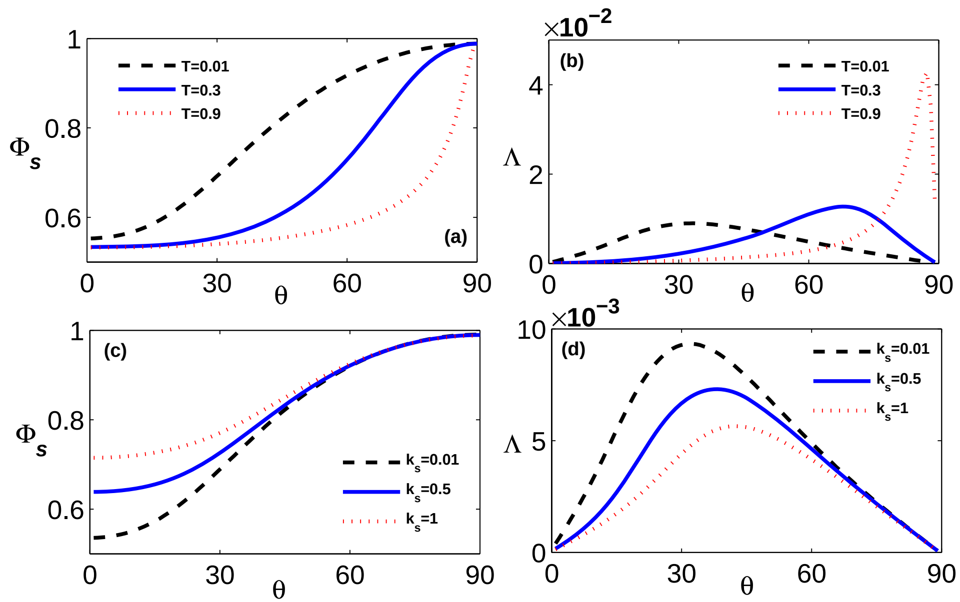
$$f_S(t) = \langle S|\chi_e(t)|S\rangle$$

$$r_c(t) = k_S \exp(-k_S t)$$

量子相变增强单态化学反应产物对磁场的敏感性

$$\Lambda(\theta) = \frac{\partial \Phi_S}{\partial \theta}.$$





单态化学反应产物 和 Loschmidt Echo （II）

有限温度下：

$$\Phi_S = \frac{1}{2} - \frac{1}{2} k_S \int_0^{\infty} L(t) e^{-k_S t} dt$$

$$f_S(t) = \frac{1}{2}\left[1 - L(t)\right]$$

$$L(t) = \prod_{k>0} \frac{A_k^2 + B_k^2}{\left[1 + \cosh\left(\beta \varepsilon_k^-\right)\right]^2},$$

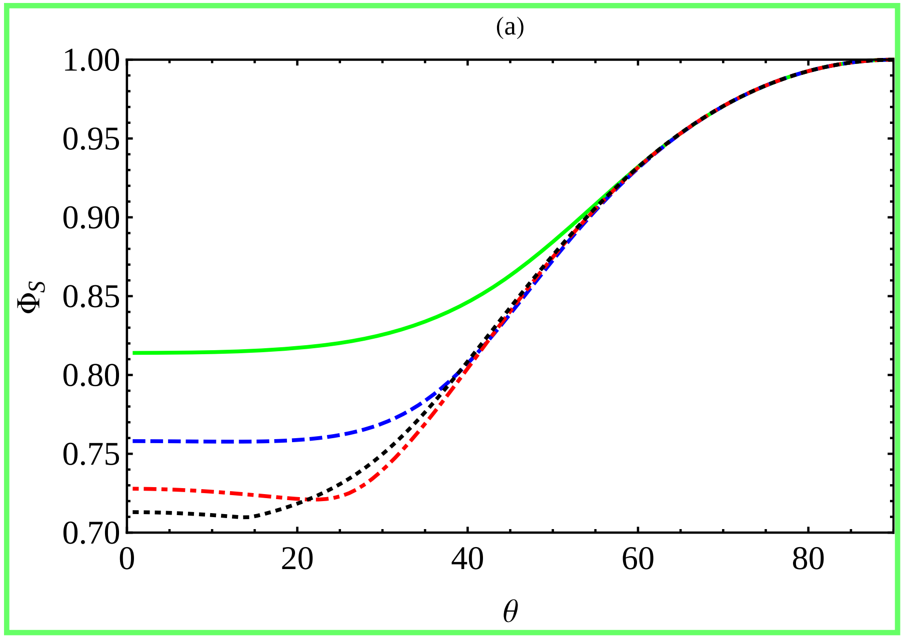
$$A_k = \left[\cos^2 \alpha_k \cos(\varepsilon_k^+ - \varepsilon_k^-)t + \sin^2 \alpha_k \cos(\varepsilon_k^+ + \varepsilon_k^-)t\right] \cosh\left(\beta \varepsilon_k^-\right) + 1,$$

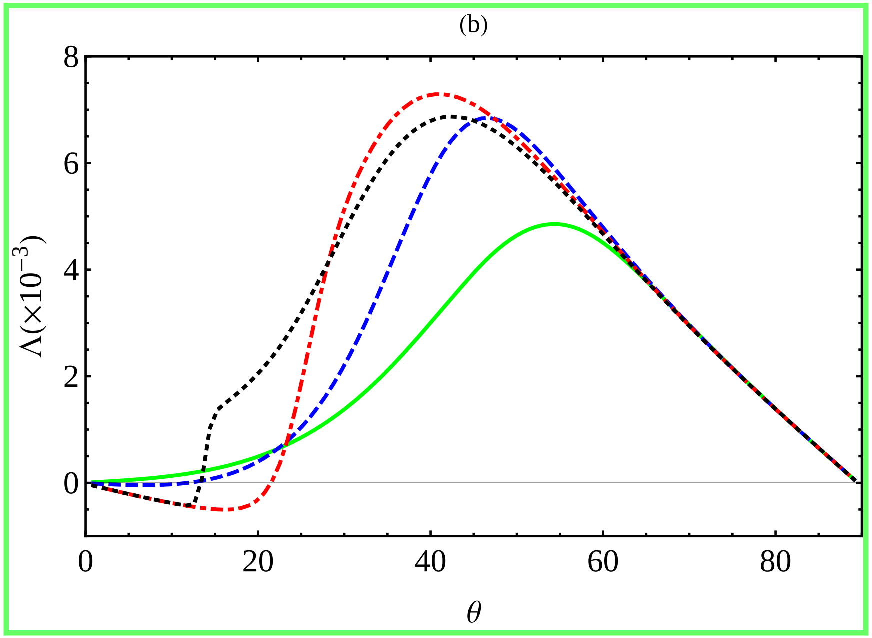
$$B_k = \left[\cos^2 \alpha_k \sin(\varepsilon_k^+ - \varepsilon_k^-)t - \sin^2 \alpha_k \sin(\varepsilon_k^+ + \varepsilon_k^-)t\right] \sinh\left(\beta \varepsilon_k^-\right),$$

$$\alpha_k = \frac{1}{2}\left(\theta_k^- - \theta_k^+\right), \qquad \theta_k^{\pm} = \tan^{-1}\left(\Delta_k / \eta_k^{\pm}\right),$$

$$\varepsilon_k^{\pm} = \sqrt{\left(\eta_k^{\pm}\right)^2 + \Delta_k^2}, \qquad \eta_k^{\pm} = \eta_k\left(\lambda_{\pm}(\theta)\right).$$

对磁场的敏感性 和 核自旋粒子数的关系





$N = 11$

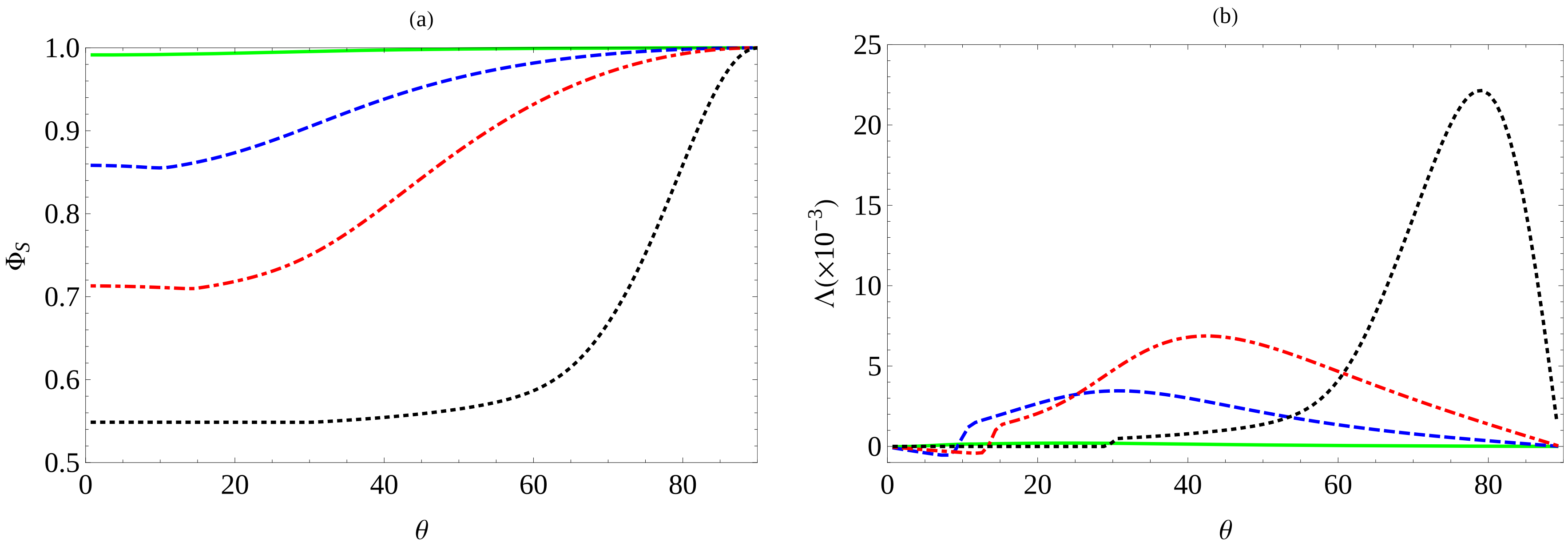
$N = 21$

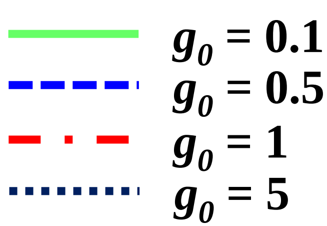
$N = 101$

$N = 1001$

核自旋粒子数越多越好

对磁场的敏感性 和 超精细耦合强度的关系

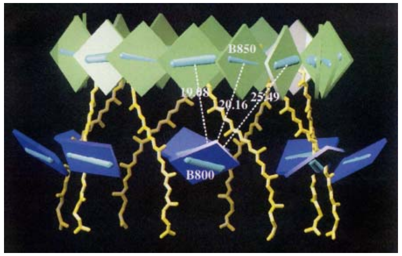


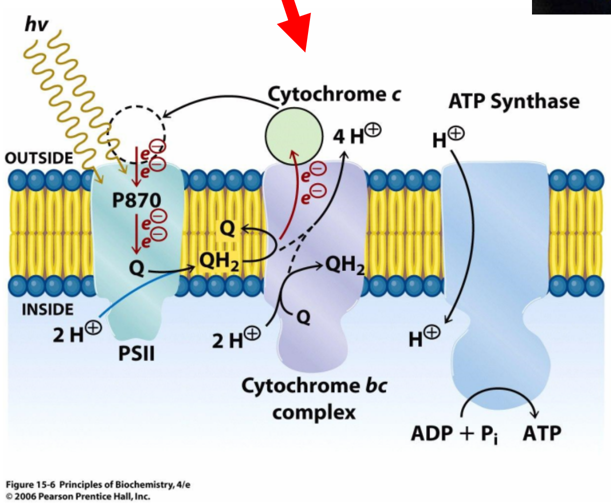


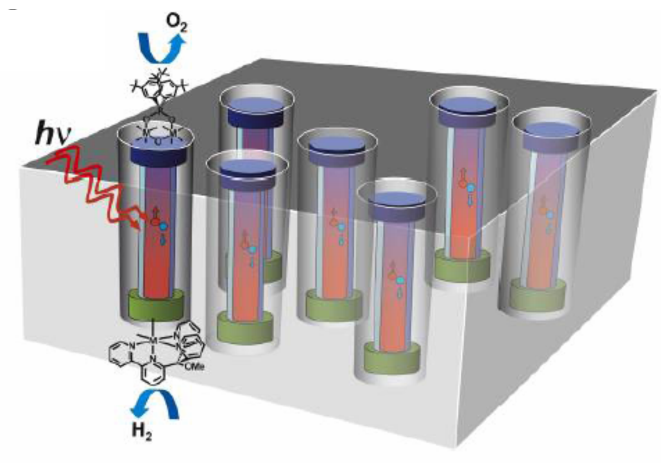
耦合强度适中最好

人工光合作用的研究

未来洁净能源的一种可能途径：发现叶绿素和光合细菌的高效传能基本机制，并用无机的人工系统模拟自然界的光合作用过程

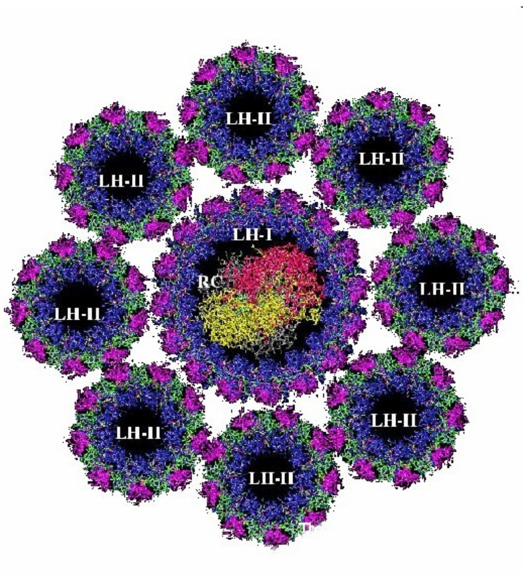


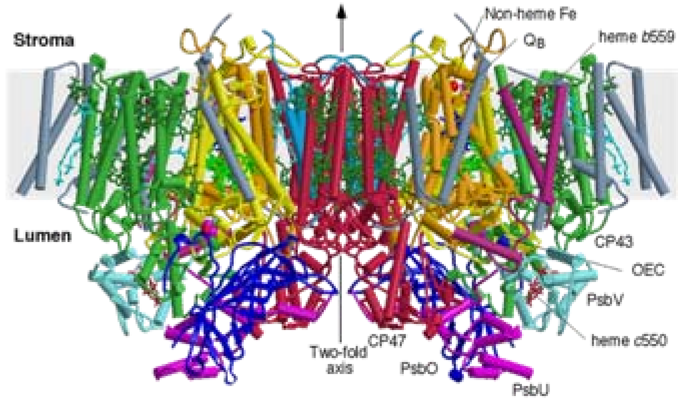




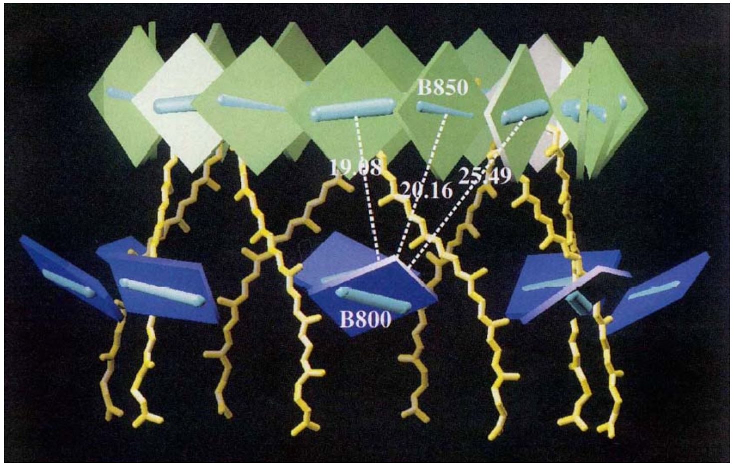
朱棣文 清华报告 2009

光合作用体 LH II 和 LH I 的基本结构



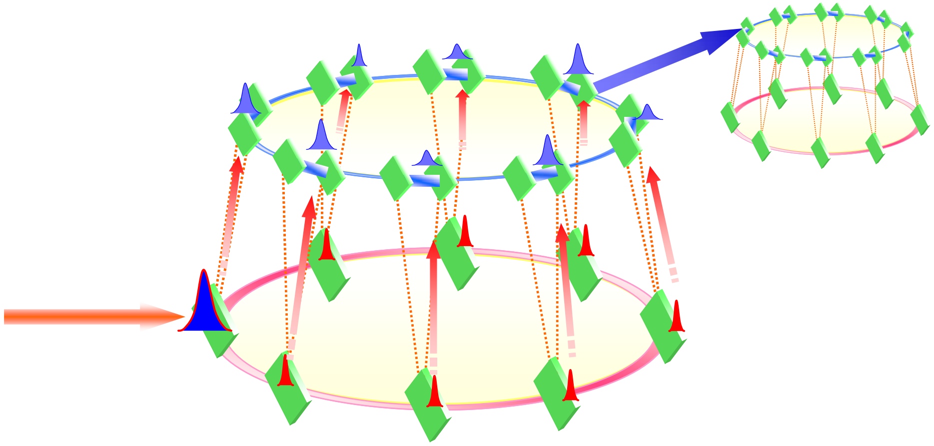


LH II 模型



purple bacteria (photosystem II)

光合作用的传能过程



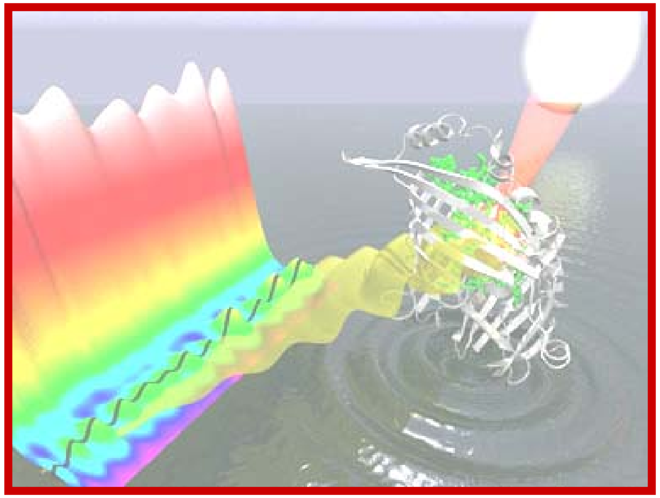
通过光激发的相干传输

重要的实验发现 1

在反应中心，单电子激发相干叠加有助于光合作用

Coherence Dynamics in Photosynthesis:
Protein Protection of Excitonic Coherence

Science 8 June 2007:Vol. 316. no. 5830, pp. 1462

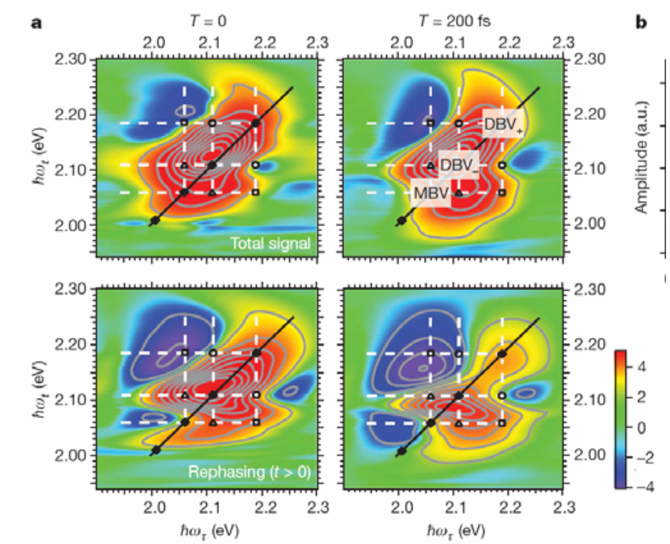


Fleming 小组，2007年在77K条件下，首次观测到光合细菌捕光天线蛋白细菌叶绿素复合体 (Fenna-Mattthew-Olson(FMO) bacteri-ochlorophyll complex) 660fs的量子相干传能

重要的实验发现 2

Coherently wired light-harvesting in photosynthetic marine algae at ambient temperature

NATURE| Vol 463|644 |2010



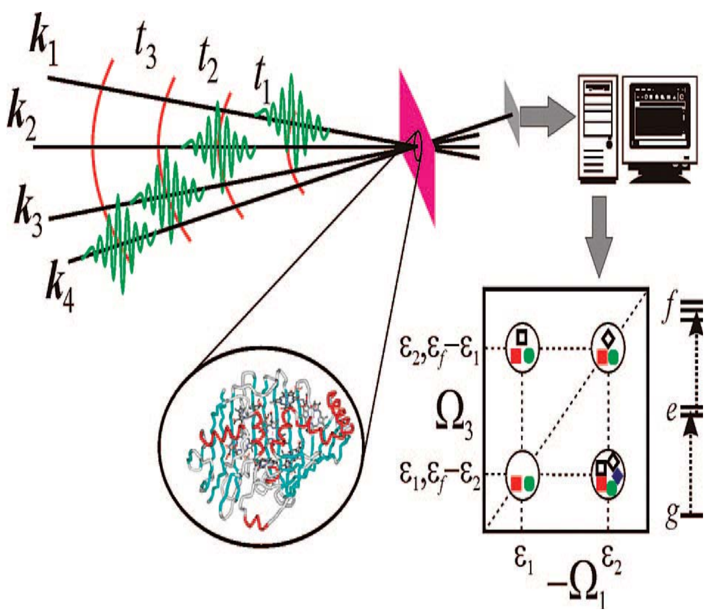
研究了常温条件下两种由隐芽海藻(marinecryptophytealgae)中提取的捕光天线蛋白(激发态的二维光子回波光谱(two Dimensional photon echo spectroscopy),获得了指 证存在量子相干叠加态的二维光谱特性

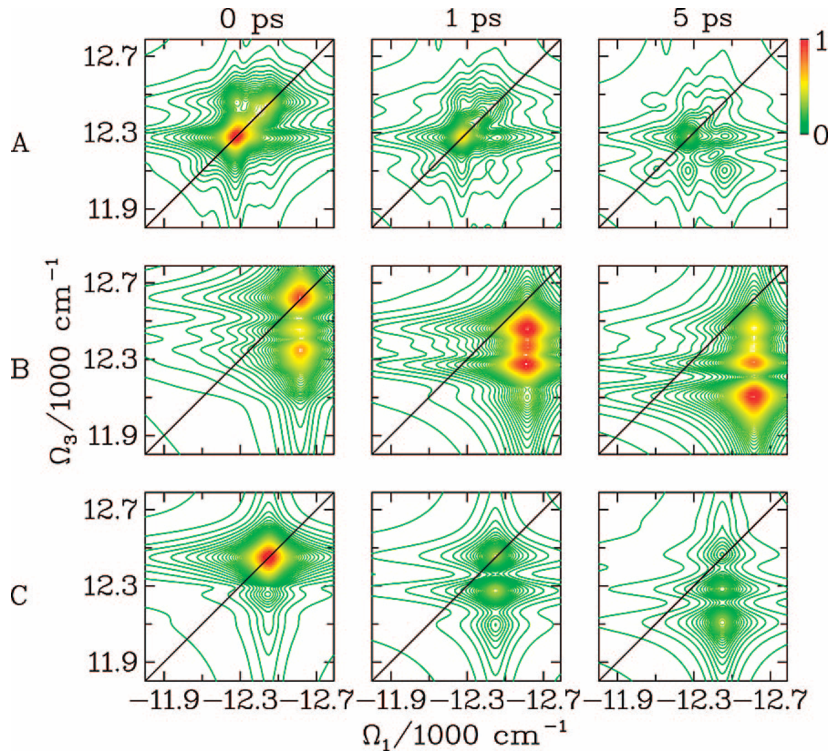
确定了持续时间至少有300fs的常温量子相干传能过程. 结果表明, 即使在生理条件下,分布于蛋白骨架不同空间位置的8个捕光色素分子(bilin,后胆色素)可以在50埃宽的空间区域内共享激发态,相干传能距离达25埃.

二维光谱技术

二维光子回波光谱

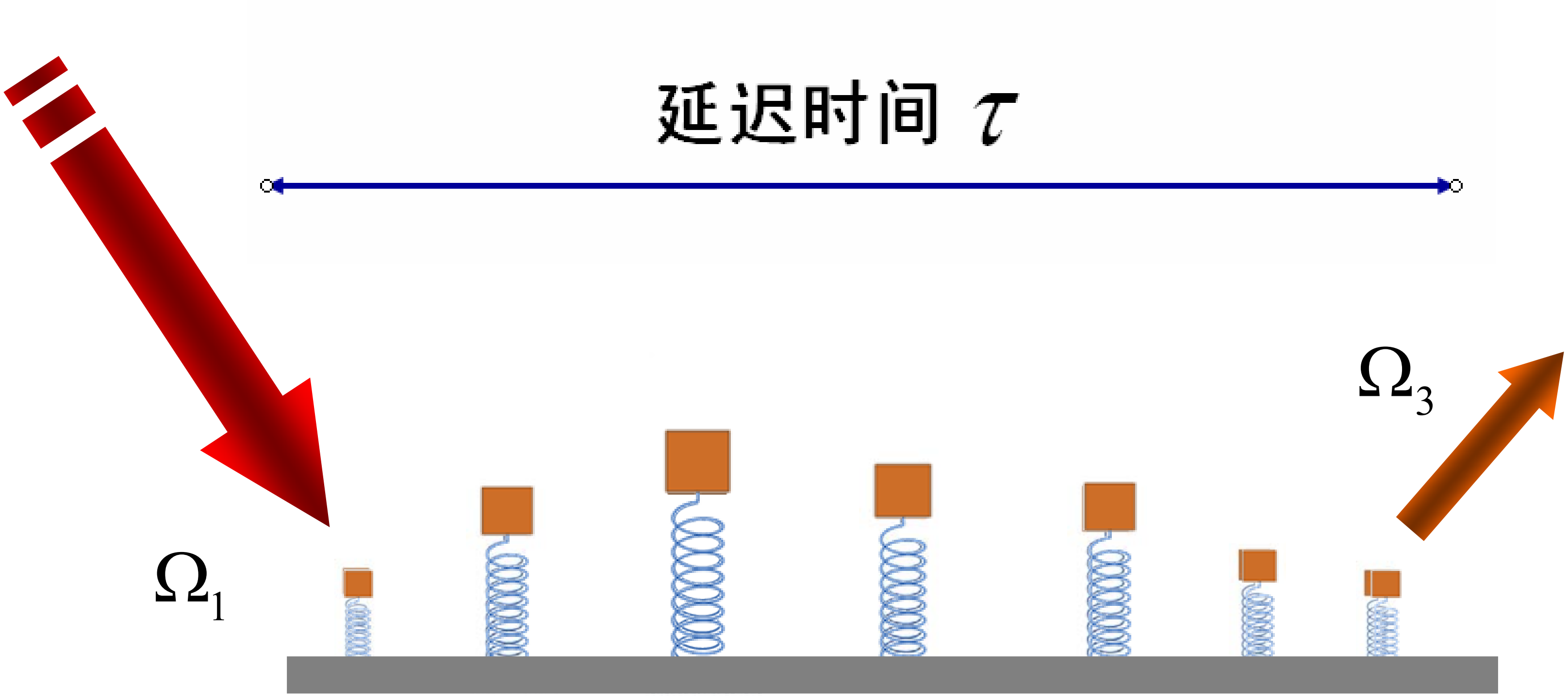
(two dimensional photon echo spectroscopy),





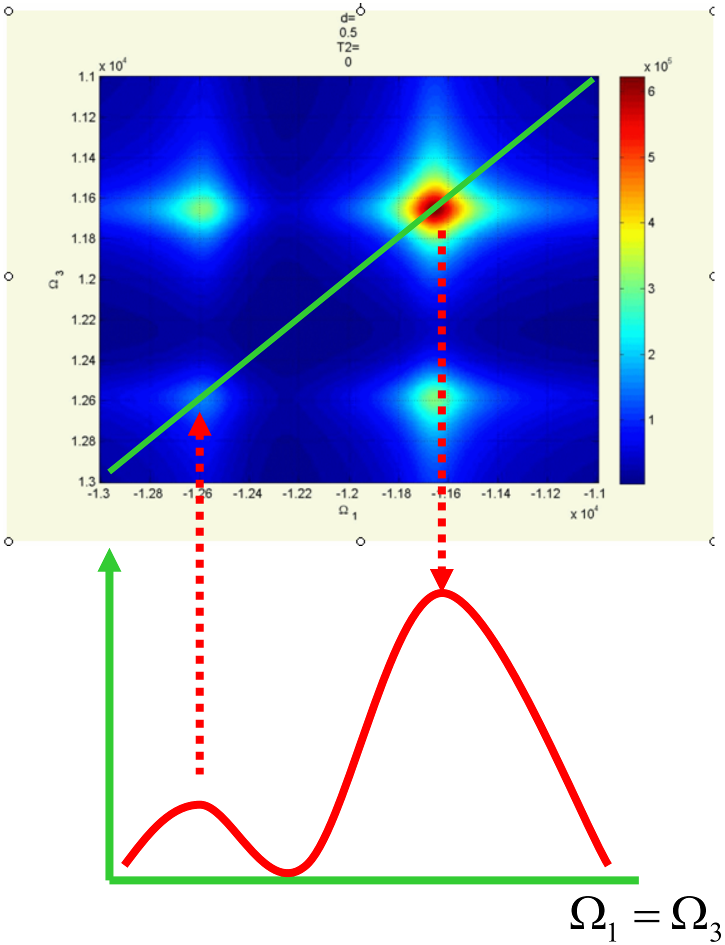
Fleming et. al, 2007

二维光谱原理示意图

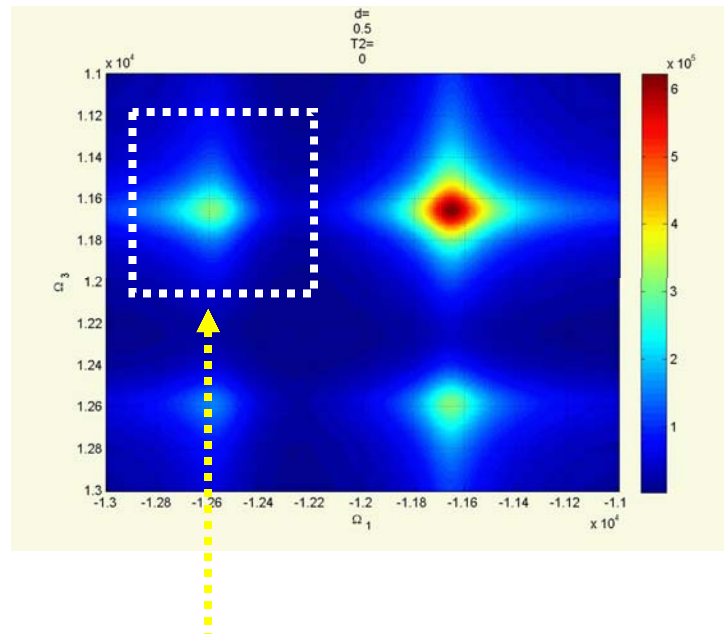


$$I_{k_s}(\Omega_3, \tau, \Omega_1)$$

二维光谱数字模拟



一维光谱

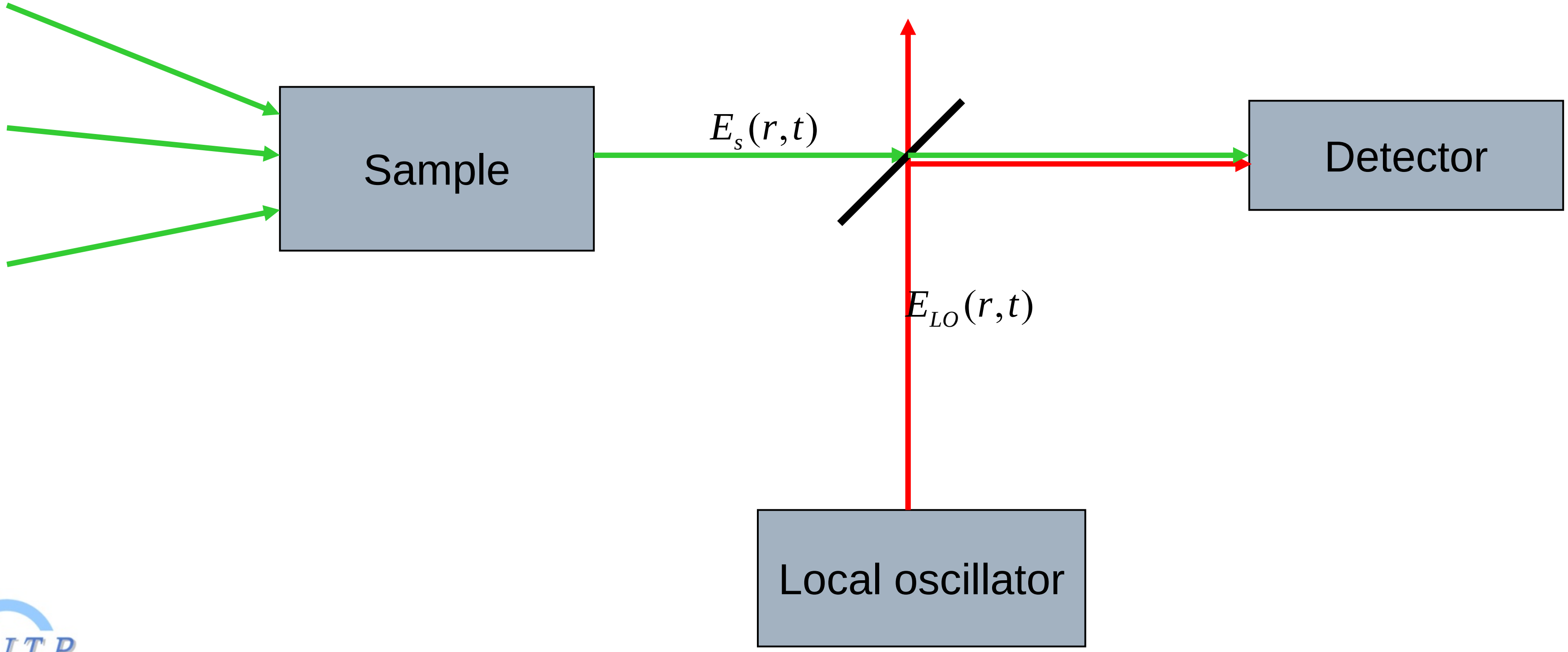


非对角项出现意味着能量转移

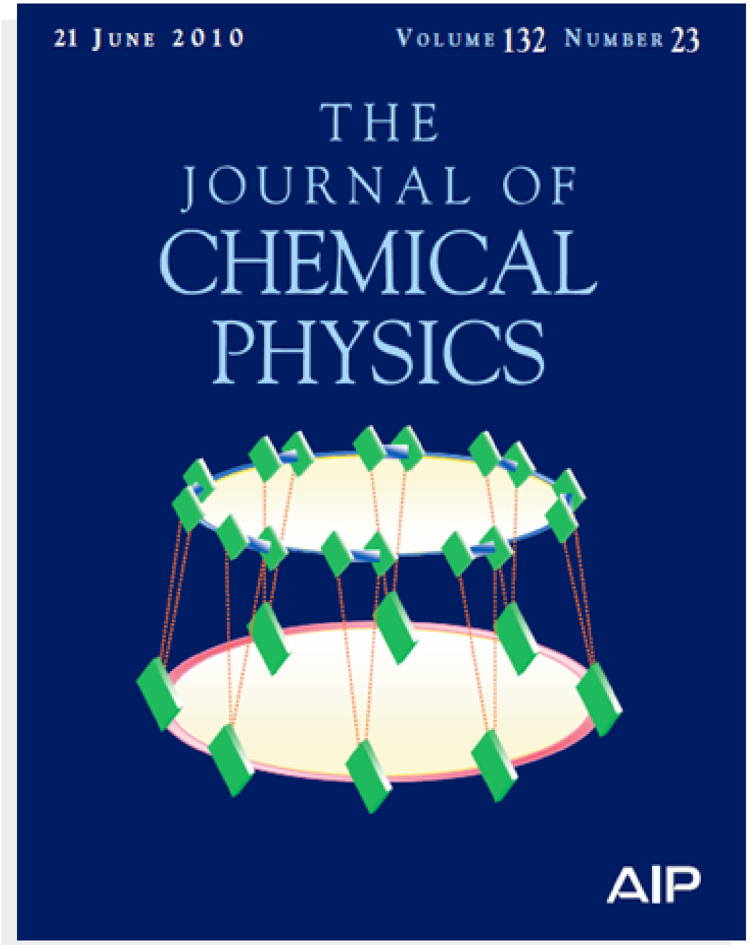
二维光谱

Heterodyne detected signal

- Experimental setup for heterodyne detection



Dimerization-assisted energy transport in light-harvesting complexes



THE JOURNAL OF CHEMICAL PHYSICS **132**, 234501 (2010)

Dimerization-assisted energy transport in light-harvesting complexes

S. Yang,[1] D. Z. Xu,[1] Z. Song,[2] and C. P. Sun[1,a)]
[1]*Institute of Theoretical Physics, Chinese Academy of Sciences, Beijing 100190, China*
[2]*School of Physics, Nankai University, Tianjin 300071, China*

(Received 20 February 2010; accepted 5 May 2010; published online 15 June 2010)

We study the role of the dimer structure of light-harvesting complex II (LH2) in excitation transfer from the LH2 [without a reaction center (RC)] to the LH1 (surrounding the RC) or from the LH2 to another LH2. The excited and unexcited states of a bacteriochlorophyll (BChl) are modeled by a quasispin. In the framework of quantum open system theory, we represent the excitation transfer as the total leakage of the LH2 system and then calculate the transfer efficiency and average transfer time. For different initial states with various quantum superposition properties, we study how the dimerization of the B850 BChl ring can enhance the transfer efficiency and shorten the average transfer time. © *2010 American Institute of Physics*. [doi:10.1063/1.3435213]

I. INTRODUCTION

To face the present and forthcoming global energy crisis, human should search for clean and effective energy source. Recently the investigations on the basic energy science for this purpose has received great attention and experienced impressive progress based on the fundamental physics.[1,2] In photosynthetic process, the structural elegance and chemical high efficiency of the natural system based on pigment molecules in transferring the energy of sunlight have stimulated a purpose driven investigation,[3–13] finding artificial analogs of porphyrin-based chromophores. These artificial systems replicate the natural process of photosynthesis[2] so that the much higher efficiencies could be gained than that obtained in the conventional solid systems.[2] It is because one of the most attractive features of photosynthesis is that the light energy can be captured and transported to the reaction center (RC) within about 100 ps and with more than 95% efficiency.[4,14]

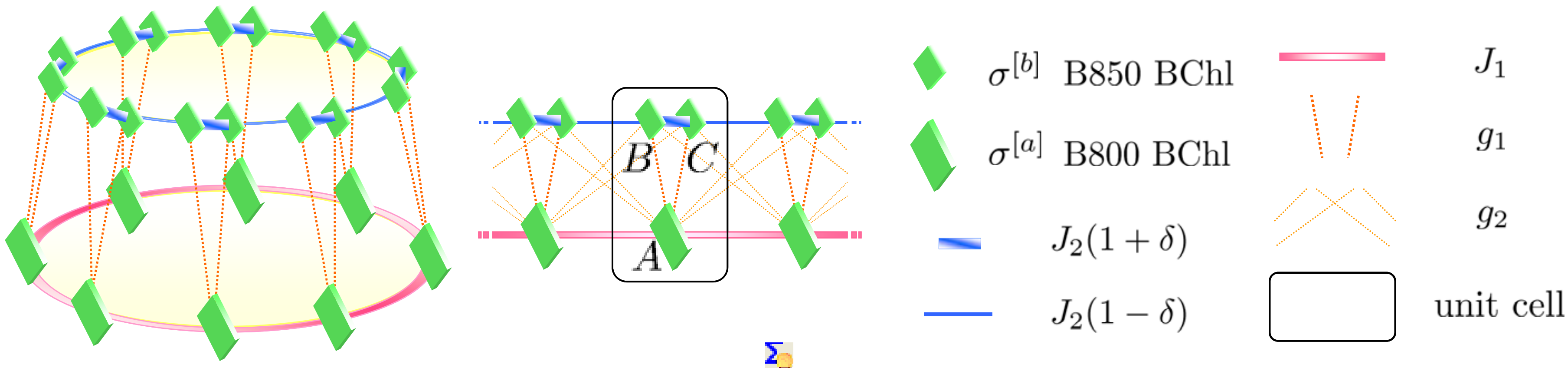
Actually, in most of the plants and bacterium, the primary processes of photosynthesis are almost in common.[3,14,15] Light is harvested by antenna proteins containing many chromophores; then the electronic excitations are transferred to the RC sequentially, where photochemical reactions take place to convert the excitation energy into chemical energy. Most recent experiments have been able to exactly determine the time scales of various transfer processes by the ultrafast laser technology.[16–18] These great progresses obviously offer us a chance to quantitatively

its induced decoherence could affect on the efficiency of the primary photosynthetic event. The present paper will similarly study the influences of spatial structure on the primary processes of photosynthesis for the light-harvesting complexes II (LH2).

In the past, by making use of the x-ray crystallographic techniques, the structure of light-harvesting system has been elucidated.[3,19] In the purple photosynthetic bacteria, there exist roughly two types of light-harvesting complexes, referred to as light-harvesting complex I (LH1) and LH2. In LH1, the RC is surrounded by a B875 bacteriochlorophyll (BChl) ring with maximum absorption peak at 875 nm. The LH2 complex, however, does not contain the RC but can transfer energy excitation to the RC indirectly through LH1. In the purple bacteria, LH2 is a ring-shaped aggregate built up by eight (or nine) minimal units, where each unit consists of an $\alpha\beta$-heterodimer, three BChls, and one carotenoid. The $\alpha\beta$-heterodimers, i.e., α-apoproteins and β-apoproteins, constitute the skeleton of LH2, while the BChls are embedded in the scaffold to form a double-layered ring structure. The top ring including 16 (or 18) BChl molecules is named as B850 since it has the lowest-energy absorption maximum at 850 nm. The bottom ring with eight BChls is called B800 because it mainly absorbs light at 800 nm. In every minimal unit, the carotenoid connects B800 BChl with one of the two B850 BChls. Excitation is transferred from one pigment to the neighbor one through the Föster mechanism,[4] while the electron is spatially transferred via the Marcus mechanism.[20] Generally, it is independent of the global geometry configuration of the system.

S. Yang, D. Z. Xu, Z. Song, CPS, JCP,132,234501(2010)

LH2 的简化物理模型

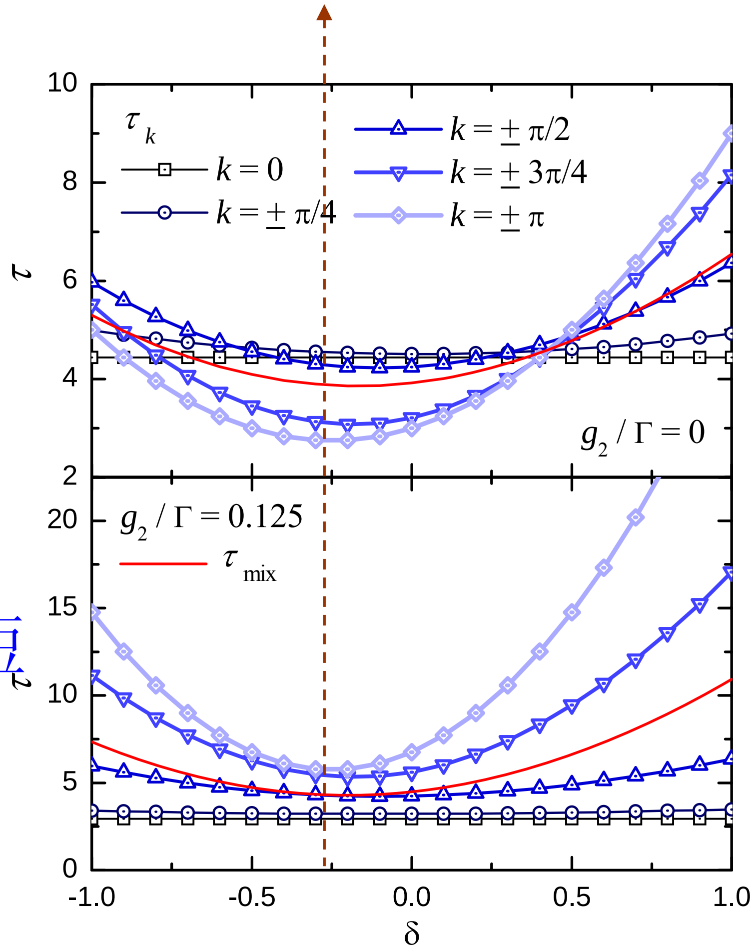


$$H_S = \sum_{j=1}^{N} \Big\{ J_1 A_j^\dagger A_{j+1} + g_1 A_j^\dagger (B_j + C_j) + \Omega_1 A_j^\dagger A_j$$
$$+\Omega_2 \left(B_j^\dagger B_j + C_j^\dagger C_j \right) + J_2[(1+\delta) B_j^\dagger C_j + (1-\delta) C_j^\dagger B_{j+1}]$$
$$+g_2 A_j^\dagger (B_{j+1} + B_{j-1} + C_{j+1} + C_{j-1}) + \mathrm{H.c.} \Big\}$$

二聚化有助于电子能量传输

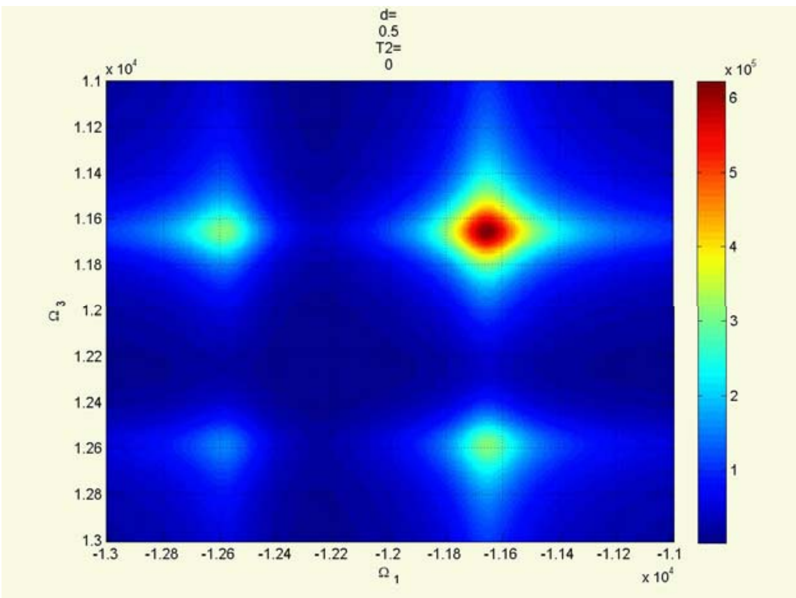
■ 二聚化时传输效率高

■ 二聚化时平均传输时间短

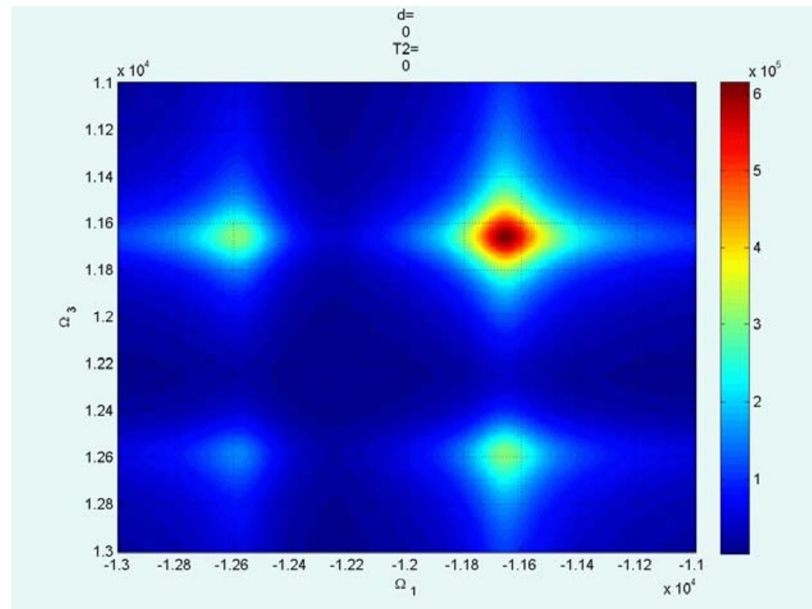


二聚化光合作用体二维光谱

- 无二聚化

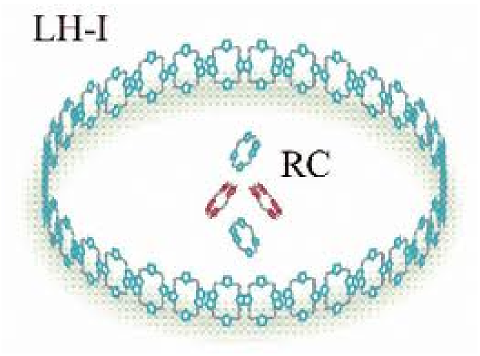


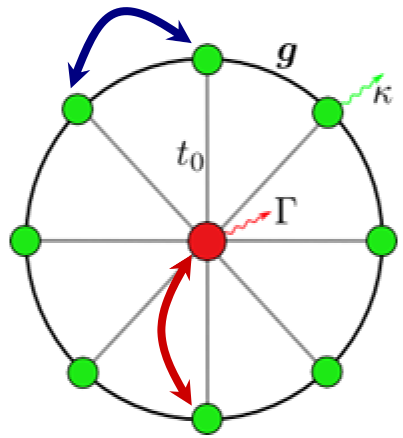
- 二聚化时传输快



ITP
The Chinese Academy of Science

LH-I Model (I)





$$H_{DA} = \sum_{i=1}^{N} \left[\epsilon e_i^\dagger e_i + \underbrace{g \left(e_i^\dagger e_{i+1} + h.c. \right)}\right]$$
$$+ \epsilon_A A^\dagger A + \sum_{i=1}^{N} \underbrace{t_i \left(e_i A^\dagger + e_i^\dagger A \right)},$$

Γ: **Usage rate of excitation** κ: **Decay rate of excitation**

A. Olaya-Castro, et al, Phys. Rev. B 78, 085115(2008)

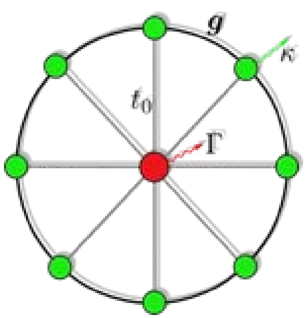
LH-I Model (II)

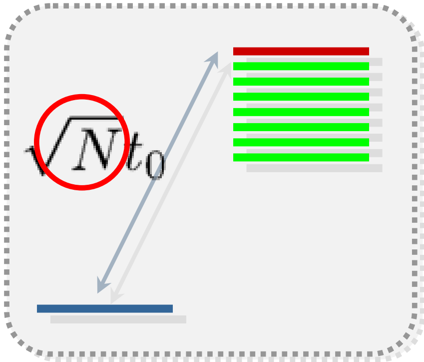
Fourier Transf: $e_j = \frac{1}{\sqrt{N}} \sum_k e^{ikj} \tilde{e}_k$

k=0 mode: $|1_{k=0}\rangle = \frac{1}{\sqrt{N}} \sum_{i=1}^{N} |1_i\rangle$

Effective Hamiltonian:

$$H_{\text{eff}}^{DA} = (\epsilon + 2g)\, \tilde{e}_0^\dagger \tilde{e}_0 + \epsilon_A A^\dagger A + \sqrt{N} t_0 \left(\tilde{e}_0 A^\dagger + \tilde{e}_0^\dagger A \right)$$





Transfer Properties

Transfer Efficiency:

$$\eta = \int_0^\infty 2\Gamma \underbrace{\left|v\left(t\right)\right|^2}_{\text{Population on Acceptor}} dt$$

Average transfer time:

$$\tau = \frac{1}{\eta}\int_0^\infty 2\Gamma t \left|v\left(t\right)\right|^2 dt$$

Average ouput power:

$$\mathcal{P} = \eta/\tau$$

ITP
The Chinese Academy of Science

A. Olaya-Castro, et al, Phys. Rev. B 78, 085115(2008)

From Donor to Acceptor

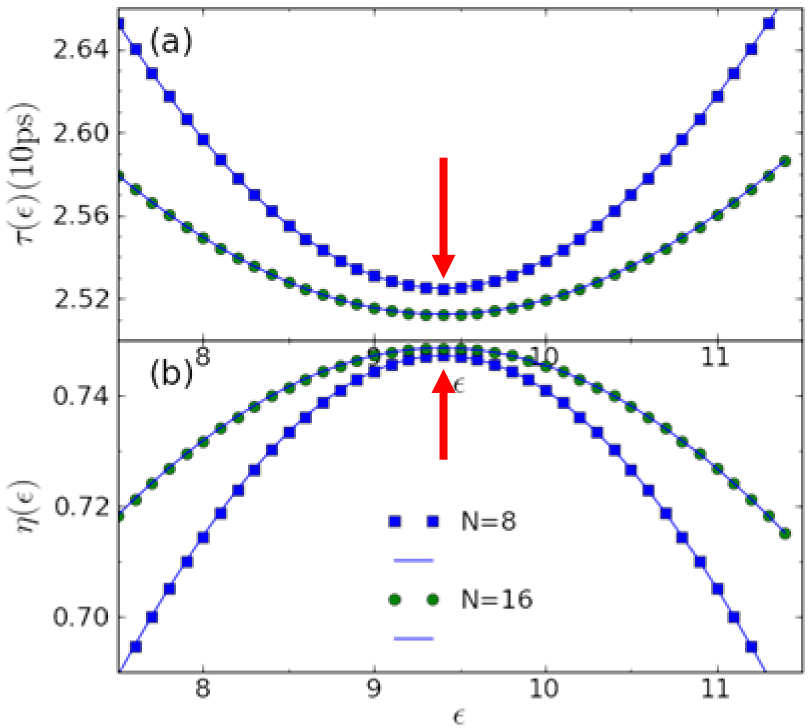
Initial Excitation on Donor ring

Optimal case:

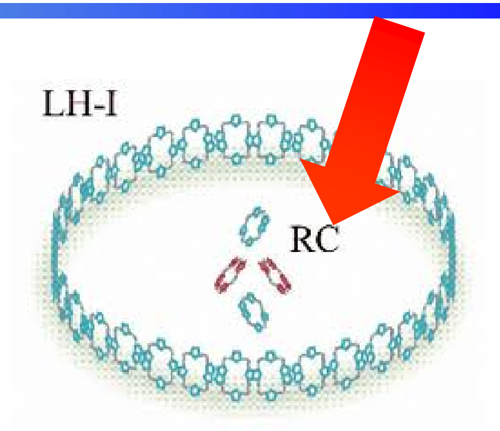
$$\epsilon + 2g = \epsilon_A$$

$\max \eta$ $\min \tau$

$$\eta_{\max} \leq \Gamma/(\Gamma + \kappa)$$



There should be light…

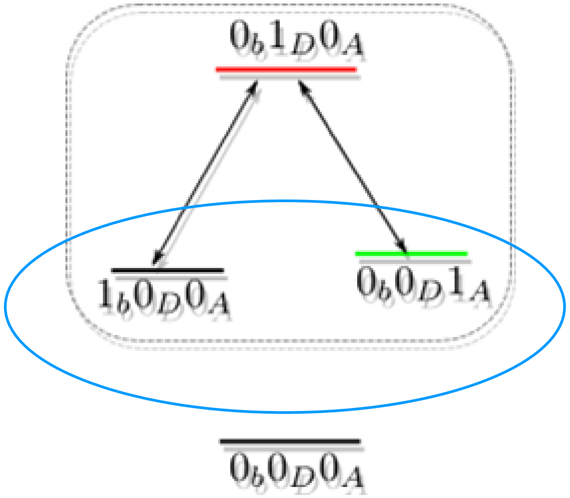


Visible light-wavelength ~ 500nm
LH-I radius ~ 4-6nm

Photon-Donor interaction:

$$H_{pD} = J\sum_{i=1}^{N}\left(e_i^{+}b + \mathrm{h.c}\right)$$

$$\begin{aligned} H_{\text{eff}} \quad = \quad & \omega_0 \tilde{e}_0^{\dagger}\tilde{e}_0 + \omega b^{\dagger}b + \omega_A A^{\dagger}A \\ & + \sqrt{N}[(t_0\tilde{e}_0^{\dagger}A + J\tilde{e}_0^{\dagger}b) + \mathrm{h.c.}] \end{aligned}$$



模拟光合作用的纳米线

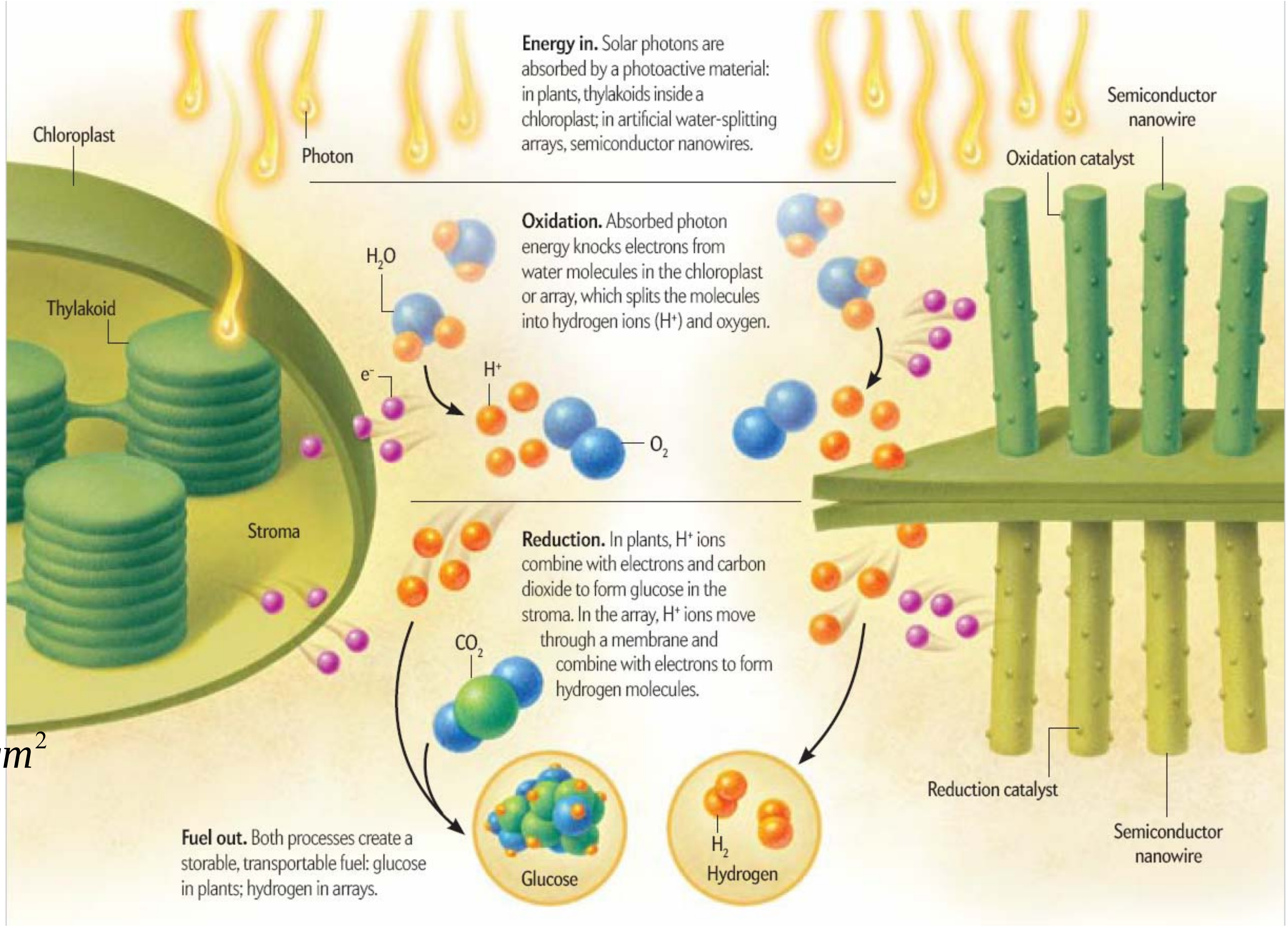
Oct.2010, ScientificAmerican.com

普通树叶

12倍

催化剂:铂

$10000 usd / cm^2$



ITP

The Chinese Academy of Science

美国能源部调研报告提出的基本能量科学的五大挑战

Phys. Today **61, July 28 (2008)**

Grand challenges in basic energy sciences

Graham R. Fleming and Mark A. Ratner

Research focused in five related areas will allow unprecedented control over the microscopic world and could be the key to a sustainable future.

1. 如何在电子水平上操控材料的物性；
2. 如何按要求设计物性并且高效合成全新的物质形态；
3. 研究如何从原子或电子的复杂关联效应中演生出来的奇妙物性，并加以控制；
4. 如何在纳米尺度上调控能量和信息，创造出可与生命物质媲美的技术；
5. 如何表征并控制非平衡态物质，特别是远离平衡态的物质。

Thank You !