

Comparison of Various Types of Coherence and Emergent Coherent Systems[†]

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Coherence is a collective property that is present in Bose–Einstein condensates (BEC), an example of which when charged is superconductivity (SC). Coherence is also believed to be present to a degree in highly efficient energy transfer in certain biological systems. Attributes of coherent systems are examined in BEC, superfluidity and Bardeen, Cooper, and Schrieffer SC and a laser in part 1. Part 2 consists of examination of various proposals for coherence including “emergent coherent systems” where there may be coherence but no phase transition. We discuss “cold” atomic gases, the Casimir effect, an extended version of Förster’s resonance

energy transfer, Fröhlich’s model, exciton-coupled quantum wells, and conceptually “old” polaritons rejuvenated by new developments. A discussion about highly efficient energy transfer in photosynthesis along with our proposal for a possible new model for this system is the last of the examples. We finish with a discussion about emergent coherent systems and attempt to classify the examples of parts 1 and 2. © 2013 Wiley Periodicals, Inc.

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Introduction

Coherence in molecular systems has evolved considerably since the fundamental insights of London,^[1] Penrose and Onsager (PO).^[2] In the 1930s, London suggested that a state that exhibited coherence would have “rigidity” in its wave function to distortions. Much later PO demonstrated how coherency ought to be reflected in a system by a macroscopic eigenvalue in the one particle reduced density matrix^[3] indicating an extensive rather than intensive quantity as a result of the entities comprising the system being in the same state with essentially the same wave function as illustrated in the caricature structures advertising this review. This is a definition of coherence, a property of a Bose–Einstein condensate (BEC), and an entity that early on existed almost exclusively in cryogenic experiments involving helium, and superconductors, and lasers.

In the last 20 or so years, there has been an experimental revolution in coherent matter studies. In 1995, the first “cold atom” experiments successfully confined a few thousand like-fermions at low enough temperatures and high enough densities to measure the elusive Bose–Einstein condensation. Today, there are at least 30 laboratories performing fascinating and precise measurements on these systems; an example would be Cornell’s observation of the Casimir effect, an effect derived from the zero point motion (ZPM) as the result of the uncertainty principle (“Oscillator Zero Point Motion, Molecular Interactions and the Casimir Effect” section).

Our interest in coherence has been generated by phase transitions driven by quasiparticles (QPs), be they magnons^[4] or a number of other species^[5] which may have coherence, so our initial discussion will be to establish fundamental attributes of established coherent systems. We discuss in detail three key concepts that should enable one to more

thoroughly appreciate and potentially contribute to the ideas. The first is the notion of a laser (“The Laser/Maser” section); a laser beam is a collection of photons (bosons) of a single wave length that can be described as a coherent state. This state has a fixed wave length (or phase) but a distribution of the number of particles; it is also over-determined, but it is a useable description of a BEC. Then, we derive the conditions required for a BEC (“Bose Einstein Condensation (BEC)/Superfluid” section). The transition temperature and statistics for suitable “cold atom” candidates are discussed.

The “Superconductivity Theory” section contains the Bardeen–Cooper–Schrieffer (BCS) theory of superconductivity. A description of the Cooper pair is first which describes how two electrons manage to bind together and behave like a boson. Nonetheless, the BCS wave function is composed of two fermions creating a coherent BEC state. Schrieffer discovered how to create a pairing operator which truncates the extended coherent state, so that it is no longer over-determined, but is normalizable and describes fermions that condense immediately after binding together if the density is high enough. The “Attributes of Coherent Systems” section fundamentals are then summarized as they will be used freely in

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the following descriptions of other models of the coherent systems proposed in "Additional Possible Examples" section.

Before discussing additional examples, we want to alert the reader that in this paragraph and later, we point out the ubiquitous presence of the harmonic oscillator which we will mention in parenthesis (HO) or a resulting dipole (D). Begin in 'Ultra-cold Atomic Gases and BEC' section with a brief outline of cold atomic gases (confined by a harmonic potential), the details of which have been covered in a number of recent reviews, books, and topical meeting summaries. Next is ZPM (of a HO) and the Casimir effect, 'Oscillator Zero Point Motion, Molecular interactions and the Casimir Effect' section, Fröhlich's coherence and energy storage/transfer proposal(s) (HO), along with critical comments and examination of a similar magnon system in 'Fröhlich's Model Coherence and Energy Transfer' section, being followed by resonance energy transfer, theory and experiment (D), 'Resonance Energy Transfer' section. 'Coherent Exciton Matter and Polaritons' section contains coherent exciton matter (D), a subject that was discussed 40 years ago, but currently is at the forefront of research due to significant experimental advances. 'Coherence in photosynthesis' section contains recent considerations about photosynthetic systems (PSs), followed by our coherent model proposal (D) and a summary of all examples. This is followed by a manuscript summary, conclusions, and proposals for future work is in 'Discussion, Conclusion, and Comments, Unanswered Questions' section. As the fields discussed cover a number of seemingly diverse topics, we have begun each section with a brief introduction. The appendices contain a very short discussion about "QPs" and "Coherence and the density matrix."

Part 1—Attributes of Coherent Systems

The laser/maser

The maser was the first engineered coherent (boson) system, operating in the microwave spectral region (predicted by Basov in 1954 and demonstrated by Ionescu in 1946)^[6]; the more familiar laser seems a better starting point to discuss a coherent system, as it also demonstrates a visual example of "phase (or mode) locking," that is, single wavelength emission such as a laser pointer. Then, the uncertainty relationship $\Delta\varphi\Delta N \sim \hbar$ says that if we have a single phase φ , we have a statistical uncertainty as to N , the number of a specific population. To build a typical device we select a suitable system (at least three distinct energy levels, suitable relaxation time, etc.^[6]), and lasing can be achieved by pumping the ground state with an intense beam of light of frequency ν_{31} to populate an excited state (level 3, Fig. 1). The rate of population is

$$\frac{dN_3}{dt} = -\frac{dN_1}{dt} = B_{31}\rho(\nu_{31})N_1(t)$$

where B_{31} is the Einstein coefficient, $\rho(\nu_{31})$ is the spectral radiant energy density and N_1 is the population of level 1. If $N = N_1 + N_3$, the maximum population that level 3 can attain in a two-level system is $0.5N$. The process labeled A_{31} is spontaneous emission, Figure 1. It proceeds independent of whether there is a radiant field or not as long as level 3 has a

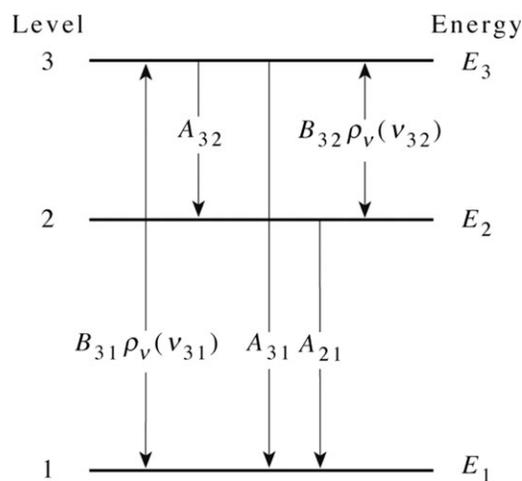


Figure 1. A simple three level energy diagram. A strong (pump) light source with frequency $\nu_{13} = (E_3 - E_1)/\hbar$ populates level 3 which can relax to level 2 or 1 by spontaneous emission or to energy level 1 by stimulated emission. Level 2 can also spontaneously emit energy and return to level 1. (Reprinted with permission from D. A. McQuarrie and J. D. Simon, *Physical Chemistry*, 1997, © University Science Books.)

population, and returns excited states to the ground state with the emission of light of frequency ν_{31} . A traditional system will lase if there is a population inversion; one method of achieving this condition is to populate level 3. Then, if light of frequency ν_{32} is emitted to populate level 2 which has a fast rate of spontaneous emission, A_{21} . Level 3 will then build population than and eventually exceed the population of level 2 (a so-called population inversion or "negative temperature") whereby an external source of light of frequency ν_{32} will enable a cascade of photons to be emitted of precisely the frequency ν_{21} . Note that an atomic system such as depicted in Figure 1 does not contain the multitude of radiationless relaxation mechanisms of molecules (see "Experimental—Fluorescence Resonance Energy Transfer" section, Fig. 12 and Ref. [7]).

Putting level 2 into an extension of the rate equation and assuming no degeneracy of all levels, the total of atoms is $N_{\text{total}} = N_1(1) + N_2(t) + N_3(t)$. At equilibrium in the kinetic processes,

$$\frac{dN_2}{dt} = 0 = A_{32}N_3 - A_{21}N_2 + \rho(\nu_{32})B_{32}N_3 - \rho(\nu_{32})B_{32}N_2$$

and rearranging, $\frac{N_3}{N_2} = \frac{A_{21} + B_{32}\rho(\nu_{32})}{A_{32} + B_{32}\rho(\nu_{32})}$

A population inversion can now be obtained if $A_{21} < A_{32}$.

For a continuous laser, the stimulated emission is reflected through the lasing medium by partially reflecting mirrors that also allow a portion of the monochromatic (ν_{32}) light to escape.

Crash course in second quantization and coherent states. In terms of second quantization operators a "raising (or creation) operator" \hat{a}^\dagger can operate on a wave function $\psi_n(x)$ containing n particles in an x coordinate system and create a new particle and changes the state to the next higher up, $\psi_{n+1}(x)$; $(n+1)^{1/2}$ is the normalization of the new wave function.^[8,9] The "lowering" (or annihilation) operator \hat{a} does the converse, so to find the number of particles in a state, these two

operators are applied in tandem creating the number operator (Table 1); its operation provides the number n of particles in a state.

Table 1. Boson operators.	
$\hat{a}^\dagger \psi_n(x) = (n+1)^{1/2} \psi_{n+1}(x)$	Raising operator
$\hat{a} \psi_n(x) = (n)^{1/2} \psi_{n-1}(x)$	Lowering operator
$\hat{a}^\dagger \hat{a} \psi_n(x) = n \psi_n(x) \quad \hat{n} = \hat{a}^\dagger \hat{a}$	Number operator
$[\hat{a}, \hat{a}^\dagger] = +1$	Boson commutator

As an example, a quantum harmonic oscillator $\hat{H}_n = \sum_n \hbar \omega \left(n + \frac{1}{2} \right)$ becomes $\hat{H}_n = \hbar \omega \left(\hat{a}^\dagger \hat{a}_n + \frac{1}{2} \right)$. Note that even if the oscillator is in the lowest vibrational mode there is a residual zero point energy (ZPE) at $T = 0$ K as a result of the uncertainty principle. A Hamiltonian with interactions can be expressed as

$$H = \sum_{\vec{q}} \epsilon b_{\vec{q}}^\dagger b_{\vec{q}} + \sum_{\vec{p}} \xi_{\vec{p}} c_{\vec{p},\sigma}^\dagger c_{\vec{p},\sigma} + \sum_{\vec{p},\vec{q}} V_{\vec{p},\vec{q}} \left(b_{\vec{q}}^\dagger c_{\vec{p}-\vec{q},\downarrow} + hc \right)$$

where the first term on the RHS is the energy of a boson, the second term is the Fermion energy, and the last term is the interaction term where two annihilation operators destroy Fermions with momentum $\vec{p} \uparrow$ and $\vec{p} - \vec{q} \downarrow$ and opposite spins and a spin zero boson with momentum \vec{q} is created. $V_{\vec{p},\vec{q}}$ is a measure of the interaction strength.

Lastly, using the ladder raising operator, we can generate all of the eigenvectors $\psi_n(x)$ by acting repeatedly on a ground state ψ_0 (here a Gaussian)

$$\psi_0(x) = \frac{1}{(n!)^{1/2}} (\hat{a}^\dagger)^n \psi_0(x)$$

Raising and lowering operators are useful in angular momentum problems such as finding the angular dependence of the various microstates of two electrons in a p^2 configuration by starting with two electrons paired in the $l = 2$ microstate; then using the lowering operator generates the other 14 microstates until the operator 'automatically' annihilates the microstate function.

A "coherent state" is:

$|\alpha\rangle = C \left[\psi_0(x) + \frac{\alpha}{1^{1/2}} \psi_1(x) + \frac{\alpha^2}{2^{1/2}} \psi_2 + \dots \right]$ where α is an arbitrary complex number and C is a normalization constant found by

$$1 = \langle \alpha | \alpha \rangle = |C|^2 \left(1 + \frac{|\alpha|^2}{1!} + \frac{(|\alpha|^2)^2}{2!} + \dots \right) = |C|^2 e^{|\alpha|^2} \text{ so } C = e^{-|\alpha|^2/2}$$

Some "useful properties" can be illustrated by writing a general coherent state as $|\alpha\rangle = e^{-|\alpha|^2/2} \left[1 + \frac{\alpha \hat{a}^\dagger}{1!} + \frac{(\alpha \hat{a}^\dagger)^2}{2!} + \dots \right] |0\rangle$ where $|0\rangle = \psi_0(x)$, the ground state and coherent state with $\alpha = 0$. Using $\exp(\hat{X}) = 1 + \frac{\hat{X}}{1!} + \frac{\hat{X}^2}{2!} + \dots$ the above equation can be written as

$$|\alpha\rangle = e^{-|\alpha|^2/2} \exp(\alpha \hat{a}^\dagger) |0\rangle$$

which are eigenstates of the ladder operator \hat{a} : $\hat{a}|\alpha\rangle = \alpha|\alpha\rangle$. Other useful properties readily follow

$$\langle \alpha | \hat{a} | \alpha \rangle = \alpha$$

$$\langle \alpha | \hat{a}^\dagger \hat{a} | \alpha \rangle = |\alpha|^2$$

Number uncertainty. The mean number operator of the quantum state $\langle \hat{n} \rangle$ is the value of $|\alpha|^2$, so the number uncertainty Δn is $\langle \hat{n}^2 \rangle = \langle \alpha | \hat{a}^\dagger \hat{a} \hat{a}^\dagger \hat{a} | \alpha \rangle = \langle \alpha | \hat{a}^\dagger (\hat{a}^\dagger \hat{a} \hat{a} + 1) \hat{a} | \alpha \rangle = |\alpha|^4 + |\alpha|^2$ using a commutation relation. Then, $\Delta n = \sqrt{\langle \hat{n}^2 \rangle - \langle \hat{n} \rangle^2} = |\alpha|$ showing that coherent states are not eigenstates of the number operator and in macroscopic coherent states, it can be shown that the mean-field value of $\hat{n} \sim \langle n \rangle$.

Phase certainty. A coherent state $|\alpha\rangle$ has a "definite phase" θ and it can be defined for any complex number α as $\alpha = |\alpha| e^{i\theta}$. Rewriting our earlier definition of α as

$$|\alpha\rangle = C \left[\psi_0(x) + e^{i\theta} \frac{|\alpha|}{1!^{1/2}} \psi_1(x) + e^{2i\theta} \frac{|\alpha|^2}{2!^{1/2}} \psi_2 + \dots \right]$$

As the ψ_n term depends on $e^{i\theta}$, we can differentiate with respect to θ and obtain

$$\frac{1}{i} \frac{\partial}{\partial \theta} |\alpha\rangle = \hat{n} |\alpha\rangle$$

As we have at least a complete set (actually overcomplete), we have the operator identity $\frac{\partial}{i \partial \theta} = \hat{n}$ (1)

So, the number and phase operators are conjugate operators related by the uncertainty principle. To emphasize coherent states have a "definite phase" but a distributed value of the number n . They are also not orthogonal in addition to being overcomplete, but they are useful in describing coherent attributes of a BEC such as a laser, and ultimately a superconducting (BCS) wave function.

Modes of a laser have a wave number \vec{k} and a circular left or right polarization, s . Hence, an occupation number representation of a state of the system is $|n_{\vec{k}_0, s_0}, n_{\vec{k}_1, s_1}, \dots\rangle$, where the \vec{k} 's count the system's plane wave states that satisfy Maxwell's equations. When quantized, each mode becomes an independent harmonic oscillator, analogous to the operators considered earlier in this section and the number operator refers to the number of photons. The operators for the independent modes commute with each other and a general coherent state can be written as

$$|\alpha_{\vec{k}_0, s_0}, \alpha_{\vec{k}_1, s_1}, \dots\rangle = e^{-\sum |\alpha_{\vec{k}_s}|^2/2} \exp \left(\sum_{\vec{k}, s} \alpha_{\vec{k}, s} \hat{a}_{\vec{k}, s}^\dagger \right) |0\rangle \quad (2)$$

where $|0\rangle$ is the vacuum state with no photons. A perfect laser would be one where only one mode was macroscopically occupied; the other modes would have zero occupation.

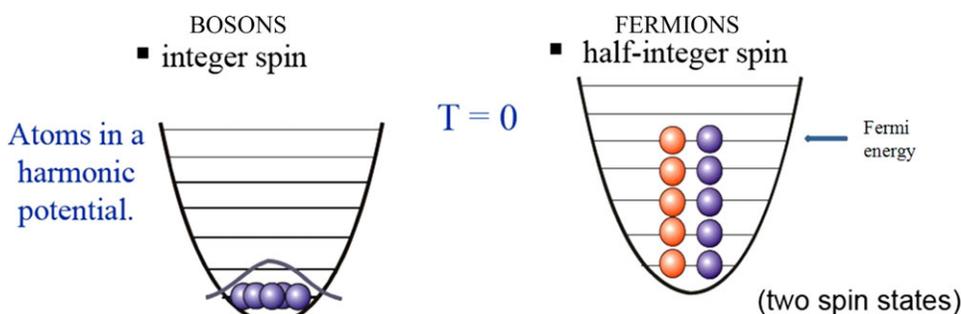


Figure 2. Illustration of bosons and fermions at $T = 0$. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Although the laser has macroscopic occupation of a single state, there is no phase transition, so strictly speaking, this is not a Bose–Einstein condensation.

Bose–Einstein condensation (BEC)/superfluid

Bosons are particles with an overall integer spin; this total includes nuclear spin as well as electron spin.^[10,11] If a nuclear spin has an odd number of protons and neutrons, the nuclear spin (I) will be a half integer. This is the case with an alkali atom, say ^7Li , then the one unpaired electron would result in a boson, as the inner electron shells are full and the orbital angular momentum and spin are zero (Unsold's theorem and $F = I \pm 1/2$). Fermions have a half integer total. At the microscopic level, these statistics are reflected in the symmetry of the many-body wave function under exchange:

$$\Psi(r_1, r_2, \dots, r_N) = \pm \Psi(r_2, r_1, \dots, r_N) \quad + = \text{Bosons and } - = \text{Fermions}$$

The dramatic nature of this effect is readily apparent in the differences in ^4He versus ^3He ; both isotopes have the same atomic spectra and are chemically equivalent, but at low temperatures, quantum fluids result; ^3He becomes a viscous liquid and a superfluid only below $T \sim 2$ mK while ^4He turns into a superfluid below $T \sim 2$ K.

At low temperatures the particle population in discrete energy levels (Fig. 2) is distinctly different. At $T = 0$ K Fermions doubly occupy the states shown with different spin states. The chemical potential that is the resistance to adding another particle is finite for Fermions at $T = 0$ K. As the temperature rises, excited particles appear above the Fermi energy, E_F and holes appear below (Fig. 3a). Contrast this with an ideal gas of bosons at $T = 0$ K where all particles will be in the lowest state "in momentum space" and the chemical potential is zero as seen in the graph below, Figure 3b. Genuine BEC is due to exchange, an idea implied by London (Eq. (5) in Ref. [12]), and further emphasized by Noziers,^[13] who also proves that the exchange interaction makes fragmentation of the condensate energetically unfavorable; hence, a BEC transition is driven by particle statistics, not their interaction. In an ideal Bose gas, at $T = 0$, all particles are in the zero momentum state, but in a real system such as helium which is interacting, there is still a macroscopic number of particles in the zero momentum state, but not all of them (Fig. 4a).

Penrose and Onsager first used the density matrix to quantify these differences: the one particle density matrix is

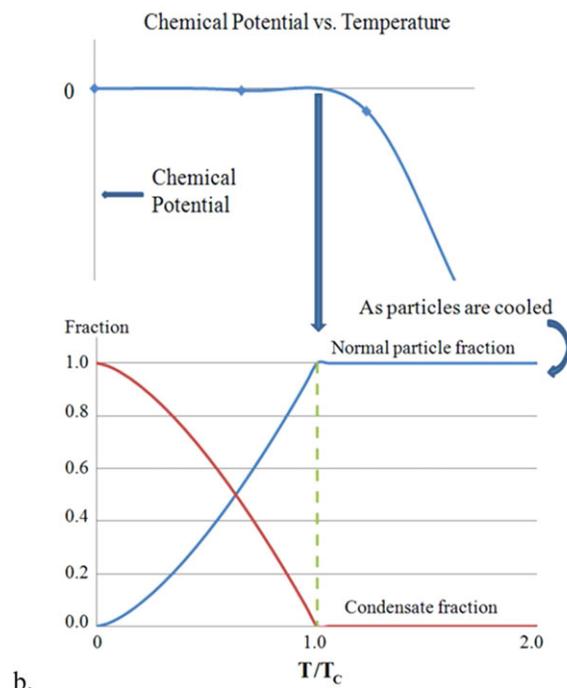
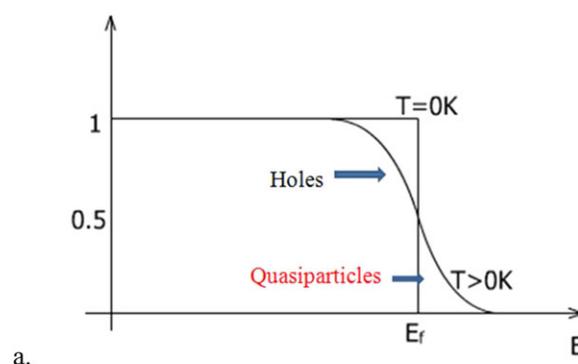


Figure 3. a) Fermi distribution as a function of T . As T is raised, QPs increase. b) When the chemical potential reaches zero, T_c is defined and BEC begins. Thus, the energy cost to add or remove a particle in an ideal BEC is zero. (See Appendix A for a brief discussion of QPs.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

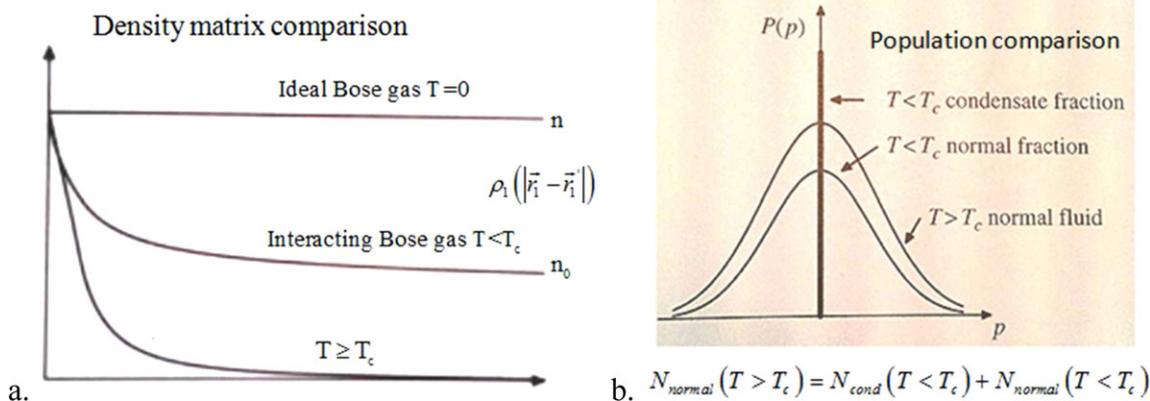


Figure 4. a) Comparison of the density matrix of ideal (noninteracting) Bose gas versus a real (interacting) Bose gas below the condensation temperature. b) Comparison of the population of the $\vec{p} = 0$ condensate fraction versus the normal state population both above and below T . (Reprinted with permission from J. F. Annett, *Superconductivity, Superfluids, and Condensates*, 2004, © Oxford University Press.) [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

$$\rho_1(\vec{r}_1 - \vec{r}_1') = N \int \Psi_0^*(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) \Psi_0(\vec{r}_1', \vec{r}_2, \dots, \vec{r}_N) d^3r_2, \dots, d^3r_N, \quad (3)$$

a correlation function between the many-body wave function at particle coordinates $\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N$ and $\vec{r}_1', \vec{r}_2, \dots, \vec{r}_N$, normalized to particle number. Integrating over all but one of the coordinates and using the symmetry of bosons, an identical result is obtained for all of the $N - 1$ particle coordinates. The density matrix only depends on the difference between $\vec{r}_1 - \vec{r}_1'$, so it has translational symmetry. Further, normalization suggests that if $\vec{r}_1 = \vec{r}_1'$ and we integrate with respect to \vec{r}_1 , we find that $\int \rho_1(0) d^3r_1 = N$, the total number of boson particles, enabling us to identify the particle number density $\rho_1(0) = \frac{N}{V} = n$. For a noninteracting ideal Bose gas at $T = 0$ comprised of single one-particle states, a many-body wave function is $\Psi_0(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \psi_0(\vec{r}_1)\psi_0(\vec{r}_2)\psi_0(\vec{r}_3)\dots\psi_0(\vec{r}_N)$. The ground state one-body density matrix is

$$\begin{aligned} \rho_1(\vec{r}_1 - \vec{r}_1') &= N \psi_0^*(\vec{r}_1) \psi_0(\vec{r}_1') \int |\psi_0(\vec{r}_2)|^2 \dots |\psi_0(\vec{r}_N)|^2 d^3r_2 \dots d^3r_N \\ &= N \psi_0^*(\vec{r}_1) \psi_0(\vec{r}_1') \end{aligned} \quad (4)$$

Assuming $\psi_0(\vec{r}) = \frac{1}{\sqrt{V}} e^{i\vec{k}\vec{r}} = \frac{1}{\sqrt{V}}$ and Fourier transforming, a zero momentum plane wave state results when condensation is in the $\vec{k} = 0$ state and the noninteracting Bose gas density matrix is equal to the particle density at $T = 0$, $\rho_1(\vec{r}_1 - \vec{r}_1') = \frac{N}{V} = n$, and all the ideal bosons can be accounted for. Again, this is not the case for an interacting system such as liquid ^4He . While the delta function represents the condensate fraction at $T < T_c$, namely the ground state at $k = 0$, the high zero point energy of helium that is present at absolute zero. Thus, helium has to be dealt with in a special manner to count all the particles. Nonetheless, even in the case of a not too strongly interacting Bose gas, a constant value n_0 is approached at large separations so a more rigorous definition for the condensate density becomes, $n_0 = \lim_{|\vec{r}_1 - \vec{r}_1' \rightarrow \infty} \rho_1(\vec{r}_1 - \vec{r}_1')$, Figure 4.

Other boson condensates can have strong interactions that destroy the condensate (more on this later).

What is required to describe the condensate is use of a method to vary the number of particles; thus, the grand canonical partition function must be used. The idea is to put our system that is a box connected to a reservoir where it takes the chemical potential μ to move a particle from the box to the reservoir. (Hence, the definition of a Green's function arises rather naturally.^[9,10,14,15]) The partition function for variable numbers of boson and fermion particles ($\sum_a n_a = N$) can be derived by modifying the classical Boltzmann statistics by subtracting μ . As

$$E = \sum_a n_a (\epsilon_a - \mu) \text{ is proportional to } e^{-\beta E} \text{ where } \beta = 1/k_B T \quad (5)$$

$$\begin{aligned} Q &= \sum_{n_1, n_2, \dots} \exp\left(-\beta \sum_a n_a \epsilon_a\right) \Rightarrow Q^\mu \\ &= \sum_{n_1, n_2, \dots} \exp\left(-\beta \sum_a n_a (\epsilon_a - \mu)\right) \\ \frac{\partial Q^{(\mu)}}{\partial \mu} &= \sum \beta \left(\sum_a n_a\right) \exp\left(-\beta \left[\sum_a n_a (\epsilon_a - \mu)\right]\right) \\ &= \sum \beta N \exp\left(-\beta \left[\sum_a n_a (\epsilon_a - \mu)\right]\right) \\ \text{but } \langle N \rangle &= \frac{1}{Q^{(\mu)}} \sum N \exp\left(-\beta \left[\sum_a n_a (\epsilon_a - \mu)\right]\right) \\ \text{so, } \langle N \rangle &= \frac{1}{\beta Q^{(\mu)}} \frac{\partial Q^{(\mu)}}{\partial \mu} = \frac{1}{\beta} \frac{\partial}{\partial \mu} \ln Q^{(\mu)} \end{aligned}$$

We find the average particle $\langle N \rangle$ as a function of μ , so that by selecting μ , we can put the number of particles we want in the box. We will apply this to BEC.

The partition function for bosons and fermions can be shown to be, Eqs. (6a) and (6b), by substituting the particle statistics (boson $n_a = 0, 1, 2, \dots$; fermion $n_1 = 0, 1$; $n_2 = 0, 1$, etc.) respectively,

$$Q_B^{(\mu)} = \prod_i \frac{1}{1 - e^{-\beta(\epsilon_i - \mu)}} \quad Q_F^{(\mu)} = \prod_i (1 + e^{-\beta(\epsilon_i - \mu)}) \quad (6a, 6b)$$

Quantum effect becomes increasingly important when the temperature T and the particle density n violate the criterion

$$n\lambda^3 \equiv \frac{nh^3}{(2\pi mkT)^{3/2}} \ll 1 \quad (7)$$

Here, when $\lambda \equiv h/(2\pi mkT)^{1/2}$, the mean thermal wavelength of the particles, approaches unity and the system is characterized by quantum effects; conversely, when $n\lambda^3 \rightarrow 0$ the system goes smoothly to the classical values. Values for liquid hydrogen and helium are 0.29 and 1.5, respectively. As this is the basis for "cold atom" BEC (section II.5), one can use the above formula to estimate the temperature needed to achieve a "cold atom" condensate for an alkali metal, roughly 10^{-7} K or so, depending on the mass.

An ideal Bose gas has the formula:

$$\frac{PV}{k_B T} \equiv \ln Q_\beta^\mu = - \sum_\varepsilon \ln(1 - ze^{-\beta\varepsilon}) \quad (8a)$$

whereas

$$N = \sum_\varepsilon \langle n_\varepsilon \rangle = \sum_\varepsilon \frac{1}{z^{-1}e^{\beta\varepsilon} - 1} \quad (8b)$$

and z is the fugacity (a measure of the deviation from ideal for a gas) related to the chemical potential as $z = \exp(\mu/k_B T)$; for all ε , $ze^{-\beta\varepsilon} < 1$. The spectrum of single particle states $\varepsilon = \hbar^2 k^2/(2m)$ is close to continuous, so the density of states $g(\varepsilon)d\varepsilon$ can be calculated as the thickness of a thin spherical shell of available states

$$g(\varepsilon)d\varepsilon = \left(\frac{2\pi V}{h^3}\right) (2m)^{3/2} \varepsilon^{1/2} d\varepsilon$$

We could integrate these equations to find (8a) and (8b), but we have excluded the $\varepsilon = 0$ level, which has statistical weight unity. Modifying Eqs. (8a) and (8b) above to include this state, taken out of the sum to give it a statistical weight of unity, leads us to

$$q(T, V, z) = \left(\frac{2\pi V}{h^3}\right) (2m)^{3/2} \int_0^\infty \varepsilon^{1/2} \ln(1 - ze^{-\beta\varepsilon}) d\varepsilon - \ln(1 - z)$$

After an integration by parts, this results in

$$q(T, V, z) = \frac{2\pi V}{h^3} (2m)^{3/2} \beta \int_0^\infty d\varepsilon \frac{\varepsilon^{3/2}}{z^{-1}e^{\beta\varepsilon} - 1} - \ln(1 - z) \quad (9a)$$

and

$$n = \frac{N}{V} = \left(\frac{2\pi}{h^3}\right) (2m)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{z^{-1}e^{\beta\varepsilon} - 1} + \frac{1}{V} \frac{z}{1 - z} \quad (9b)$$

When $z \ll 1$, the system is classical; when z is close to unity, the last term in Eq. (9b) is identical to N_0/V where N_0 is the particle number for the $\varepsilon = 0$ level. This term can become a large fraction of the particle density $n = N/V$ leading to a Bose-Einstein condensation (BEC). The last

term in Eq. (9a) can be dropped from consideration, as $z/(1 - z) = N_0 \Rightarrow z = N_0/N_0 + 1$; so, $-\ln(1 - z)$ will be neglected for all values of z . The integrals above are evaluated by substitution of $x = \beta\varepsilon$ and result in the general expression:

$$g_n(z) = \frac{1}{\Gamma(n)} \int_0^\infty \frac{x^{n-1}}{z^{-1}e^x - 1} \quad 0 \leq z \leq 1 \quad \Gamma(n) \text{ is the Gamma function}$$

In terms of this function, our previous equations are now

$$q(T, V, z) = \frac{V}{\lambda^3} g_{5/2}(z) \quad \text{and} \quad N(T, V, z) = \frac{V}{\lambda^3} g_{3/2}(z) + N_0(z) \quad (10a, 10b)$$

These are not straightforward functions to evaluate, so to make progress, we expand the integrands that must be less than or equal to one (specifically z), so they converge (first multiply by $\frac{ze^{-x}}{ze^{-x}}$, then expand the denominator):

$$\frac{1}{z^{-1}e^x - 1} = ze^{-x} \frac{1}{1 - ze^{-x}} = ze^{-x} \sum_{p=0}^\infty (ze^{-x})^p = \sum_{p=1}^\infty z^p e^{-px}$$

Now, we can evaluate:

$$\begin{aligned} g_n(z) &= \frac{1}{\Gamma(n)} \sum_{p=1}^\infty z^p \int_0^\infty x^{n-1} e^{-px} dx = \frac{1}{\Gamma(n)} \sum_{p=1}^\infty \frac{z^p}{p^n} \int_0^\infty y^{n-1} e^{-y} dy \\ &= \frac{1}{\Gamma(n)} \sum_{p=1}^\infty \frac{z^p}{p^n} \{\Gamma(n)\} = \sum_{p=1}^\infty \frac{z^p}{p^n} = g_n(z) \end{aligned}$$

Writing Eq. (10b) as:

$$N(T, V, z) = \frac{V}{\lambda^3} g_{3/2}(z) + N_0(z) = N_{\text{ex}} + N_{\varepsilon=0},$$

there are two limiting conditions

$$1 = \frac{N_{\text{ex}}}{N} + \frac{N_{\varepsilon=0}}{N} \quad \lim_{N \rightarrow \infty} \left\{ \begin{array}{l} 1 = \frac{N_{\text{ex}}}{N}, \frac{N_{\varepsilon=0}}{N} = 0 \\ 1 = \frac{N_{\text{ex}}^{\text{max}}}{N} + \frac{N_{\varepsilon=0}}{N} \end{array} \right\} \quad (11)$$

The top limit is for fugacity $z < 1$ and all the particles occupy the excited states; the bottom limit for $z = 1$ (see Fig. 3b). Then, the excess condenses in the ground state ($\varepsilon = 0$) when

$$\frac{N\lambda^3}{V} = n\lambda^3 = g_{3/2}(z) = n \left(\frac{2\pi\hbar^2}{mk_B T}\right)^{3/2}$$

Inverting this equation, we can find the chemical potential μ and at high T or low density n , the small $g_{3/2}(z)$ expansion gives (see Fig. 3b)

$$\mu \sim -\frac{3}{2} k_B T \ln \left(\frac{mk_B T}{2\pi\hbar^2 n^{2/3}} \right)$$

When $z = 1$, the chemical potential is zero and for fixed density n , we obtain the BEC temperature:

$$T_c = \frac{2\pi\hbar^2}{k_B m} \left(\frac{n}{2.612} \right)^{2/3} \quad (12)$$

Interacting particles

Returning to Eq. (4), we expand this equation for a general interacting particle case where

$$\lim_{|\vec{r}_1 - \vec{r}_2| \rightarrow \infty} \rho_1(\vec{r}_1 - \vec{r}_1) = \begin{cases} n_0 \rightarrow T < T_c \\ 0 \rightarrow T \geq T_c \end{cases} \quad (13)$$

as illustrated in Figure 4. We can define the probability that a particle is in a region of momentum space as d^3p by the expectation value ($T = 0$) by $P(\vec{p})d^3p = \frac{Vd^3p}{(h)^3} \langle \Psi | \hat{n}_{\vec{k}} | \Psi \rangle$ where $\hat{n}_{\vec{k}}$ is the number operator for state \vec{k} , $|\Psi\rangle$ is the N-body wave function, $Vd^3p/(h)^3$ is number of states in the d^3p momentum region, and $\vec{p} = \hbar\vec{k}$. The expectation value is a Fourier transform of the one-body density matrix $n_{\vec{k}} = \langle \Psi | \hat{n}_{\vec{k}} | \Psi \rangle = \int \rho_1(\vec{r}) e^{i\vec{k}\cdot\vec{r}} d^3r$. From Eq. (13), we can write the behavior of $\rho_1(\vec{r}) = n_0 + \Delta\rho_1(\vec{r})$; after the Fourier transform this expression is

$$n_{\vec{k}} = \int n_0 e^{i\vec{k}\cdot\vec{r}} d^3r + \int \Delta\rho_1(\vec{r}) e^{i\vec{k}\cdot\vec{r}} d^3r = n_0 V \delta_{\vec{k},0} + f(\vec{k}) \quad (14)$$

The condensate is represented by the delta function ($\vec{k} = 0$); if $\vec{k} \neq 0$, it is zero. The Fourier transform $f(\vec{k})$ goes to zero large \vec{r} and it should be continuous at $\vec{k} = 0$ and symmetric.

Relating this description to the two fluid model of liquid helium, there are two components of the mass flow, \vec{j}_s the superfluid mass (sometimes called "particle current") density, and the normal fluid current density \vec{j}_n . The total current is the sum of the flows, $\vec{j} = \vec{j}_s + \vec{j}_n = n_s \vec{v}_s + n_n \vec{v}_n$ where the \vec{v}_s are the respective velocities. Here, the normal component carries all of the entropy, as the superfluid condensate is a single many-body state and by definition, the entropy is zero. We can write the momentum distribution for this case from Eq. (14) as

$$P(\vec{p}) = n_0 V \delta(\vec{p}) + \frac{V}{(2\pi\hbar)^3} f\left(\frac{\vec{p}}{\hbar}\right)$$

The two contributions are from the condensate $n_0 V$ (delta function) and the remaining $N - n_0$ particles.

At room temperature classical Boltzmann statistics apply as the distinction between bosons and fermions gets "washed out."^[16] Convincing arguments have been presented that BEC can only occur in 3D.^[17] However, Kosterlitz, Thouless, and Berezinski have surmised that 2D vortex structures can exist,^[18,19] and these have been found in low-temperature studies of liquid helium in a matrix. However, instead of the long-range order (Fig. 3a), the decay of coherence of the SF is now algebraic, $1/r^{\eta(T)}$, as discussed by Nelson.^[20] Additional studies by Bagneto and Kleppner^[21] demonstrate that low-dimensional condensation can occur, if there is a special confining potential geometry, which suggested a possible method of isolating and condensing cold gases prior to their discovery (see Ref. [22] for details, especially Fig. 9).

Superconductivity theory (BCS)

There are at least four key pieces to the BCS theory.^[23] The only interactions in a simple electron gas are Coulomb repulsions; superconductivity requires an attraction to create electron pairing but what type of particles can do this? To date a number have been proposed,^[5b] but it was first suggested by Fröhlich's showed how such an attraction V could arise through an electron-phonon interaction; the theory predicted a mass effect that was soon verified. However, this model was one dimensional and several years passed until second, Leon Cooper found a bound state.^[24] With the premise of an attraction of strength V , Cooper diagonalized numerous very large matrices representing many different M -body problems with an attractive interaction between the electrons

$$\hat{H}_{\text{pair}} = \begin{pmatrix} 2\varepsilon & -V & -V & \cdot \\ -V & 2\varepsilon & -V & \cdot \\ -V & -V & 2\varepsilon & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix} \hat{H}^T = \begin{pmatrix} 2\varepsilon - nV & 0 & 0 & \cdot \\ 0 & 2\varepsilon + V & 0 & \cdot \\ 0 & 0 & 2\varepsilon + V & \cdot \\ \cdot & \cdot & \cdot & \cdot \end{pmatrix} \quad \text{--- } \frac{V}{(m-1)V} \quad (15)$$

in an $M \times M$ matrix with the results that $m - 1$ degenerate levels are always raised in energy by V , and a single nondegenerate level, the Cooper pair, is lowered in energy as a multiple of the number of interactions, $(m - 1)V$. All M electron pairs that scatter have the same momentum and are within $\hbar\omega_D$ of the Fermi energy ε_k , giving maximum correlation while obeying the exclusion principle as regards the filled lower levels. Thus, there is an attractive energy V between electrons (mitigated by the lattice phonons for small values of \vec{k}), a bound state (negative energy) emerges from the continuum (eq (8)), composed of electrons in excess of the Fermi energy. Further, no matter how small V is, it is always larger than the kinetic energy, thus the Fermi surface is unstable. The binding energy is not analytic at $V = 0$, so Cooper's result cannot be obtained by perturbation theory.

Third, Schrieffer wrote a wave function that was a coherent state of electron pairs using the pairing operator $\hat{P}_{\vec{k}}^\dagger = \hat{c}_{\vec{k}\uparrow}^\dagger \hat{c}_{-\vec{k}\downarrow}^\dagger$ which creates a pair with zero momentum and opposite spins.^[23,25] He constructed a variational many-body wave function $|\Psi_{\text{BCS}}\rangle = \text{const} \cdot \exp\left(\sum_{\vec{k}} \alpha_{\vec{k}} \hat{P}_{\vec{k}}^\dagger\right) |0\rangle$ and used the complex numbers $\alpha_{\vec{k}}$ as variational parameters. As the pairing operators commute and $(\hat{P}_{\vec{k}}^\dagger)^2 = 0$, the coherent state becomes a product of exponentials for each \vec{k} point and

$$|\Psi_{\text{BCS}}\rangle = \text{const} \cdot \exp\left(\sum_{\vec{k}} \alpha_{\vec{k}} \hat{P}_{\vec{k}}^\dagger\right) |0\rangle = \text{const} \cdot \prod_{\vec{k}} \left(1 + \alpha_{\vec{k}} \hat{P}_{\vec{k}}^\dagger\right) |0\rangle,$$

as all terms containing $\hat{P}_{\vec{k}}^\dagger$ in quadratic and higher terms vanish. With this feature, the wave function can be normalized:

$$1 = \langle 0 | \left(1 + \alpha_{\vec{k}}^* \hat{P}_{\vec{k}}\right) \left(1 + \alpha_{\vec{k}} \hat{P}_{\vec{k}}^\dagger\right) |0\rangle = 1 + |\alpha_{\vec{k}}|^2 \text{ and written as}$$

$$|\Psi_{\text{BCS}}\rangle = \prod_{\vec{k}} \left(u_{\vec{k}}^* + v_{\vec{k}}^* \hat{P}_{\vec{k}}^\dagger\right) |0\rangle \quad \text{with} \quad u_{\vec{k}}^* = \frac{1}{1 + |\alpha_{\vec{k}}|^2}, v_{\vec{k}}^* = \frac{\alpha_{\vec{k}}}{1 + |\alpha_{\vec{k}}|^2}, \quad (16)$$

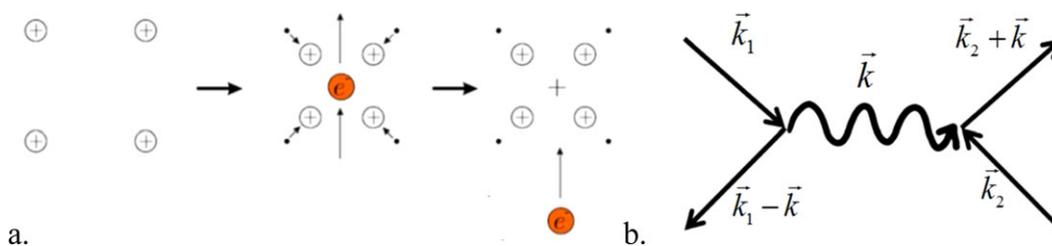


Figure 5. a) As the much faster electron passes through the lattice, it creates a positively charged lattice deformation that attracts another electron. b) The quantum electrodynamic view is that two electrons exchange a virtual boson (here, a phonon with momentum \vec{k}). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Here, v_k is the probability for finding a pair occupied and u_k is the probability a pair is unoccupied; the normalization is $|u_k|^2 + |v_k|^2 = 1$. If we redefine the reference state as the Fermi sea at $T = 0$ (all states $k < k_F$ occupied; the rest empty), then we can write a symmetrized hole-pair BCS wave function (Fig. 6):

$$|\Psi_{\text{BCS}}\rangle = \prod_{k > k_F} (u_k^* + v_k^* \hat{p}_k^\dagger) \prod_{k' < k_F} (u_{k'}^* P_{k'} + v_{k'}^*) |\psi_0\rangle \quad (17)$$

The original manipulation of the Schrieffer wave function is somewhat convoluted; Schrieffer has simplified it and it is described in detail^[25].

Lastly, Bardeen quickly recognized that these two discoveries are the missing pieces of the superconducting theory based on his previous work in which he had experimentally bounded the content a viable SC theory needed to have. There can be no doubt that there is quantization on a macro-scale based the ensuing experiments. Deaver and Fairbank^[26] and Doll and Naubauer^[27] placed a hollow cylinder composed of superconducting material in a slowly increasing magnetic field. The cylinder only absorbs a quantized magnetic flux of energy $\Phi = hc/2e$ and confirmed London's prediction that superconductivity is a macroscopic quantum phenomenon,

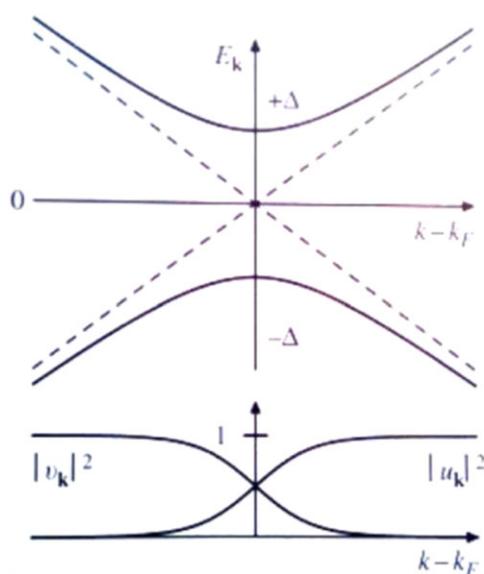


Figure 6. View of a symmetrized hole-pair BCS wave function (see text for details).

but the superconducting state is a single-valued quantum state with charge $2e$, not $1e$. The superconducting state is also a perfect diamagnet, completely excluding the flux from an external magnetic field until absorption of precisely one quantum of energy. How the perfect diamagnetic state is reached is independent of path (see Figs. 7a and 7b), so it must be a phase transition, albeit a special one with a macroscopic wave function with a single phase that "breaks" the electromagnetic field symmetry,^[28] a prototype for the Higgs mechanism. Cooper pairs form and immediately undergo BEC. A summary of the macroscopic BCS attributes is listed:

1 "Cooper pairs" underpin a superconductor that has the property of resistance-free conduction of an electric current. Using the experimental setup in Figure 7a, after a SC current has been established and the magnetic field removed, the current flowed for years at $T < T_c$ with no apparent dissipation.

2 To approach a macroscopic description, BCS theory must be done in real space using $\Delta^*(\vec{r}) = V \langle \hat{\psi}_\uparrow^\dagger(\vec{r}) \hat{\psi}_\downarrow^\dagger(\vec{r}) \rangle$, which is analogous in behavior to a wave function with charge $2e$. Gorkov^[29] showed that $\Delta(\vec{r})/T_c \approx \psi(\vec{r})$, is a "macroscopic wave function"; in addition $\psi(\vec{r})$ is also a complex order parameter for the thermodynamic Ginzburg–Landau (GL) free energy theory (useful for discussing phase transitions) where F_N and F_S are the normal and superconducting free energies in the expression (an expansion in even terms of ψ):

$$F_S = \int d^3r \left[\alpha |\psi|^2 + \frac{1}{2} \beta |\psi|^4 + \frac{1}{2m} |(-i\hbar\nabla - 2e\vec{A})\psi|^2 + \frac{(\vec{B} - \vec{B}_0)^2}{2\mu_0} \right] + F_N \quad (18)$$

The first two terms inside the brackets are from the Landau theory, the next two terms are the coupling to the electromagnetic field where $2e$ is the charge and \vec{A} is the vector potential, and the last term is the magnetic field energy. Leaving out some details, Eq. (11) is minimized with respect to ψ , and defining a current

$$\vec{j} = \frac{\partial F}{\partial \vec{A}} \Rightarrow j_s = \frac{ie\hbar}{m} (\psi^* \nabla \psi - \psi \nabla \psi^*) - \frac{4e^2}{m} \vec{A} \psi^* \psi, \quad (19)$$

the latter term representing a quantum current. If $T > T_c$, $\alpha > 0$ and the order parameter $|\psi| = 0$. When $T < T_c$, a phase

Flux Quantization Experiments

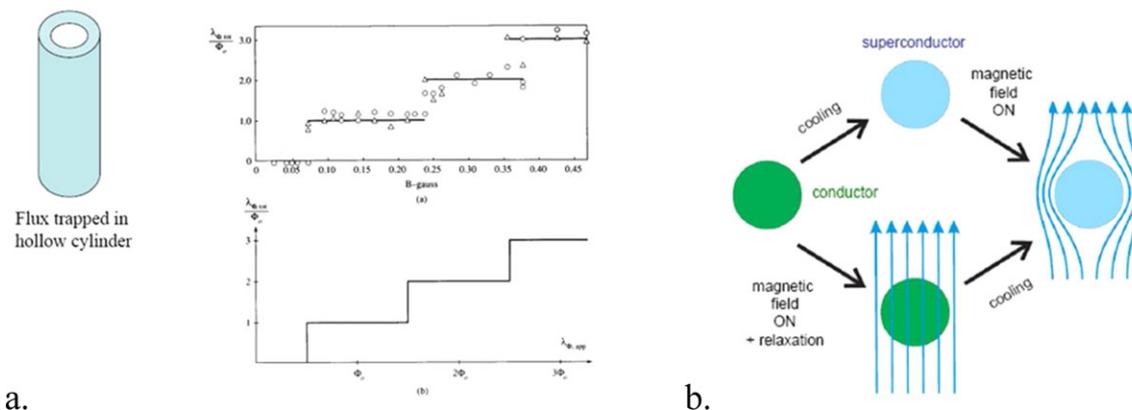


Figure 7. a) Flux quantization experiment. b) Two different paths to an identical superconducting state. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

transition occurs and the order parameter ψ becomes finite and if there is no magnetic field, $\vec{B} = 0$, $|\psi| = \sqrt{-\alpha/\beta}$. Using a complex order parameter $\Phi(\vec{x}) = \sqrt{n_0(\vec{x})}e^{i\tilde{S}(\vec{x})}$, $n_0 = -\alpha/\beta$, and substituting into the current equation $\vec{j}_s = \frac{2e}{m}n_0(\hbar\nabla\tilde{S} - 2e\vec{A})$, and choosing the right (London) gauge for $\vec{A} \rightarrow \vec{A} - \frac{\hbar}{2e}\nabla\tilde{S}$ we arrive at the London equation

$$\vec{j}_s = \frac{4e^2}{m}n_0\vec{A} \quad (20)$$

Then,

$$\begin{aligned} \nabla \times [\text{Eq. (13)}] &= \nabla \times \vec{j}_s = -\frac{4e^2}{m}n_0\nabla \times \vec{A} \\ &= -\mu_0\nabla^2\vec{B} = -\frac{4e^2}{m}n_0\vec{B} \end{aligned}$$

and we have an equation for magnetic screening that results in the Meissner effect providing perfect screening, which means the material is a perfect diamagnet (London proves this in Ref. [1]). A solution is $\vec{B}(\vec{x}) = \vec{B}_0e^{-z/\lambda_L}$ (where z is perpendicular to the SC surface) results in

$$\frac{1}{\lambda_L^2} = \frac{\mu_0 n_0 4e^2}{m}$$

If the magnetic field is B_0 at the boundary of the superconductor, it will only penetrate the “London penetration depth” λ_L into the superconductor. London further connected the penetration depth with the phase stiffness of the particular superconductor (see later).

Writing the condensate wave function as $\psi(\vec{r}, t) = \sqrt{n_0(\vec{r}, t)}e^{i\tilde{S}(\vec{r}, t)}$ and assuming the phase and amplitude are allowed to vary over long distances and removing the field from Eq. (12), it can be shown that the current is proportional to the gradient of the phase, $\vec{j} = \frac{\hbar}{m}n_0\nabla\tilde{S}$; a difference in phase will generate a superfluid flow. If the density and temperature are constant, as the curl of a gradient is zero, we have

$\nabla \times \vec{j} = -\frac{\hbar}{m}n_0\nabla \times (\nabla\tilde{S}) = 0$. This suggests that the condensate density does not change, the liquid is irrotational, and if we enclose a pole of the SC wave function inside a loop, we have $\oint_L \vec{j} \cdot d\vec{l} = N(\frac{\hbar}{m}n_0)$, where N is the number of vortices. Vortices can be a method of dissipation of superconductivity coherence.

The solution of the GL theory for $B = 0$ gives two length scales: (1) the penetration depth of the magnetic field into the superconductor $\lambda = \sqrt{\frac{m\beta}{4\mu_0e^2|\alpha|}}$ and (2) the coherence length

$$\xi = \sqrt{\frac{\hbar^2}{2m|\alpha|}}$$

The thermodynamic GL theory provides valuable insight into the phase change from superconducting to the normal state, especially in the presence of a magnetic field. The BCS theory provides a “macroscopic wave function.”

1. Shortly after the BCS theory was published, Josephson^[30] predicted that if two superconductors were separated by an insulating barrier, the SC current (Cooper pairs) can tunnel through the normal barrier if it is not too thick. The effect is based on the fact that the phase difference between the two superconductors creates a potential difference,

$$\partial(\Delta S)/\partial t = 2eV/\hbar, \quad (21)$$

the current is powered by the phase difference. At his initial seminar presentation, there were those skeptical of the graduate student’s work,^[31] which was proved experimentally with help from Anderson and Rowell.^[32] Josephson^[33] wrote a very clear review shortly after his extraordinary discovery that is currently a major field of research.

2. There is a connection between a weakly bound BCS Cooper pair “boson” and a more tightly bound BEC. Nozieres and Schmitt-Rink^[34] showed how a hole-pair (exciton), Eq. (10), could continuously traverse from BCS to the BEC side and the size of the Cooper pair diminishes, respectively. The BCS wave function is viable for both sides, and Refs. [34] and [35] contain many more details.

Table 2. BEC characteristics.

A macroscopic fraction of the particles are in the same quantum state. An ideal BEC undergoes a phase transition. The condensation of particles is in momentum space and is similar to an extended matter wave (single phase) which "breaks" electromagnetic symmetry. Two condensates interacting should interfere with each other, one test for coherence. The condensate has a macroscopic eigenvalue in the one-particle reduced density matrix indicating long-range spatial order. As a superconductor's "boson" is composed of two highly correlated electrons, it also has off-diagonal long-range order (ODLRO) in the two-particle reduced density matrix, where the off-diagonal term represents the interaction forming the Cooper pair 'quasiboson.' ('Quasiboson' as the electron pair still obeys the Pauli principle, but acts like a boson.)

There is a complex order parameter $\Phi(\vec{x}) = \sqrt{n_0(\vec{x})}e^{iS(\vec{x})}$, which can be used as a connection to thermodynamics (specifically the GL equation). Superfluidity has flow without friction and an energy gap for elementary excitations. The flow is proportional to the gradient of the phase, $\vec{v}_s(\vec{x}, t) = \frac{\hbar}{m}\nabla S(x)$ and it is irrotational, that is, $\nabla \times \vec{v}_s(\vec{r}) = 0$.

Vortices are quantized on traversing a path around a nonsuperfluid object, $\oint \nabla S(x) \cdot d\vec{s} = 2n\pi$ analogous to the quantization of a charged superconductor; the phase may change only in multiples of 2π along a closed path.

The energy associated with London's "phase stiffness" (ρ_s) can be expressed as $H_s = \rho_s \int d^3r (\nabla S)^2$, which measures resistance to twisting; S is the phase of the SC or SF.

Josephson's junction $\partial(\Delta S)/\partial t = 2eV/\hbar$ illustrates the dependency of the current flowing between two SC's on the phase difference between them.

For completeness of the table, coherence does not seem to necessarily require a phase change (laser).^[36] A broader definition of coherence is called spontaneous emergence of coherence (SEC), which can be applied to small, coherent groups of QPs. Various recent studies suggest a phase change may not result, but then symmetry breaking must happen, which can indicate a collective mode. See Sppendix B for a brief discussion of QPs and more discussion will follow ("Discussion, Conclusion, and Comments, Unanswered Questions" section).

Part II—Additional Possible Examples

Ultracold atomic gases and BEC

This subject has grown exponentially in the last 15 or so years and a good introduction can begin with a review of atomic spectroscopy.^[22,37] I find that students can be rather quickly intrigued by the subject and brought to appreciate a research effort in a standard physical chemistry course. And Charlene Moore's famous atomic energy tables contain some interesting opportunities. The BEC theory thus far presented will be used, and there seem to a number of computational opportunities. To begin, a pair of alkali atoms with a single unpaired electron (inner electrons are a closed shell with a total angular and spin momentum of zero) could become a boson and perhaps condense. "All" that is required is to trap and cool the atoms "sufficiently" (10^{-7} K or so), which took decades to achieve. One difficulty is the coupling of the electronic and the nuclear spins, which could lead to $S = 1$ or $S = 2$ bosons. The spin substates will separate in the presence of a magnetic field. It turns out that the magnetic field will also create a magnetic "trap" for lower energy atoms, while the higher energy atoms remove energy, thus create a cooling effect on the remaining atoms. A decade of additional work resulted in the first atomic gas BEC in 1995. Properties experimentally observed in helium have also been verified in atomic BECs; the particles in the BEC state neither contribute to the pressure of the gas nor participate in heat transfer, and the viscosity at $T \leq T_c$ drops orders of magnitude. As we know that these BECs have interactions, the

Schrödinger equation can be modified to include the magnetic trap and a nonlinear interaction term, and the resulting equations are called the Gross-Pitaevskii equations^[38–40]:

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V_{\text{trap}}(\vec{r}) + NV_{\text{eff}}|\Psi(\vec{R})|^2\right)\Psi(\vec{R}) = E_N\Psi(\vec{R}) \quad (22)$$

The potential of interaction $V_{\text{int}} = \frac{4\pi\hbar^2 a}{M}$, where a is the scattering length and M , the atomic mass, is a mean-field between the atoms which multiplies the nonlinear term and results in significant consequences. If $a > 0$, the interaction being repulsive and the BEC disperses, whereas $a < 0$ (attractive interaction) causes the BEC to collapse, so the scattering length is crucial to forming a stable BEC. As illustrated in Figure 8, using a magneto-optical trap and getting a high enough density allowed the textbook momentum space view of cold atom BEC.

Again there is the debate whether true coherency can happen in a mesoscopic system without BEC. Cold atom BEC has attributes of coherence such as the interference of condensates, but no truly macroscopic phase transition (in the thermodynamic limit). Based on other systems and models

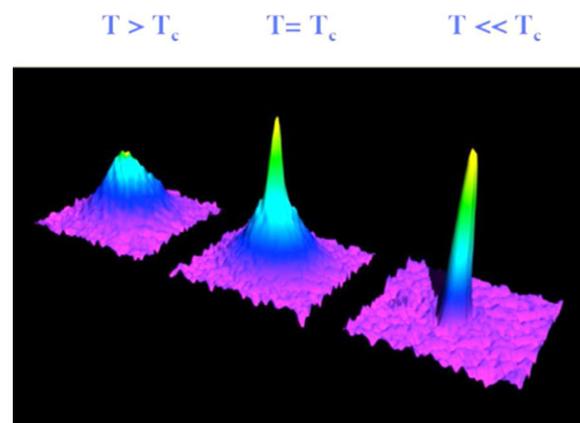


Figure 8. Momentum space view of cold atom BEC (from Ref. [22]); compare with Figure 3b. Figure is reprinted with permission from Ketterle, W. (2002) Rev Mod. Phys. **74**, 1131, Copyright (2004) by the American Physical Society. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

discussed, it seems that conditions for coherence without macroscopic condensation might be more prevalent than previously thought; we will discuss this point in the conclusions.

Oscillator ZPM, molecular interactions and the Casimir effect

While the origin of the van der Waals attraction for molecules with a permanent electric dipole was understood before London's work, the experimentally determined correction for gases like helium was not.^[41–43] To derive this dispersion relationship (named after him), London used a model which allowed him to separate the interaction of two nonexcited molecules into six uncoupled oscillators, see Eq. (5).^[12] He identified the third term of this equation as an attractive interaction, $\varepsilon = -\frac{3\hbar\nu_0\alpha^2}{4R^6}$, where α is the polarizability, and R is the distance between the two molecules. Further, he makes the point that this effect is connected with the presence of a quantum ZPM with energy $\hbar\omega/2$; otherwise there would be no interaction energy as oscillators at rest do not mutually polarize each other if they do not have an inherent multipole.^[12] This insight is one difference between infrared and Raman spectroscopy.^[44]

Later, with guidance from Bohr about ZPE,^[45] Casimir^[46] derived a macroscopic formula for the force/area between two plates, independent of the material properties of the plates $F(d)/A = \frac{\pi^2\hbar c}{240d^4}$. He was motivated by experimental results, which showed that the force drops off faster (R^{-7}) than London's prediction at distances larger than 10 nm. At this distance, the finite speed of light (called "retardation") must be taken into account. Casimir and Polder then calculate the interaction between an atom and a surface, now referred to as the Casimir–Polder (CP) Effect.^[47] Both of these effects depend on the geometry of the interacting bodies. Only recently have experimental advances been made that can allow accurate measurements. Lifshitz used the following substitution to allow for thermal excitation of N zero point modes:

$$\frac{\hbar\omega}{2} \rightarrow \frac{\hbar\omega}{2} + \langle n_{\text{mean}} \rangle = \frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\hbar\omega/k_B T} - 1} \quad (23)$$

Here, $\langle n_{\text{mean}} \rangle$ is the mean level of excitation of an oscillator at temperature T . Putting the last term of Eq. (16) over a common denominator, we can account for the Lifshitz temperature correction in a closed form ($\beta = 1/k_B T$):

$$\begin{aligned} \frac{1/2\hbar\omega\{\exp(\beta\hbar\omega) - 1\} + \hbar\omega}{\exp\{\beta\hbar\omega\} - 1} &= \frac{1/2\hbar\omega\{\exp(\beta\hbar\omega)\} + 1/2\hbar\omega}{\exp\{\beta\hbar\omega\} - 1} \\ &= \frac{1/2\hbar\omega\{\exp(\beta\hbar\omega) + 1\}}{\exp\{\beta\hbar\omega\} - 1} = 1/2 \frac{\{\exp(\beta\hbar\omega) + 1\}}{\exp\{\beta\hbar\omega\} - 1}; \end{aligned}$$

now multiply by $\frac{\exp\{-\beta\hbar\omega/2\}}{\exp\{-\beta\hbar\omega/2\}}$ and let $x = \frac{\hbar\omega}{k_B T}$, then $= \frac{\hbar\omega}{2} \left(\frac{e^{x/2} + e^{-x/2}}{e^{x/2} - e^{-x/2}} \right) = \frac{\hbar\omega}{2} \coth x$ where \coth is the hyperbolic cotangent.

If the thought of two conducting plates seems a bit bizarre, an interesting article by Kleppner discusses this effect using

identical LC circuits, also harmonic oscillators,^[48] and several interesting examples of the effects. Lamoreaux also considers the Casimir effect and recent advances in understandable terms^[49] and scholarpedia. One interesting measurement that captures two topics contained in this manuscript is the measurement of the CP effect in a cold atomic system.^[50] The quantum electrodynamics view is that the Casimir effect is also due to the exchange of virtual bosons (photons). For additional details, see Salam^[42] and Milton.^[51]

Fröhlich's model coherence and energy transfer

From the 1960s through the 1970s, Fröhlich's developed and refined a kinetic model of coherence in biological systems based on dynamic momentum space correlations that he suggested might result in a BEC.^[52–54] The overall idea is that as a biological molecule and its surroundings have a high electric field (order 10^5 V/cm), the huge dipole inherent in these systems could be pumped by an energy source. If these systems interact synergistically, they could be elevated into a single metastable state that may develop coherence if the state's energy relaxation rate were lower than an exciting energy source much like the laser in "The Laser/Maser" section, Figure 1. Further, Fröhlich's suggested that as water sometimes surrounds a biological molecule in a rather static position and water also has a transparency at frequencies of the order of $10^{10} - 10^{12}$ Hz, the relaxation route might be considerably slower. "Frozen" water molecules (or any other relatively static surroundings) could be a key component in some systems, especially, as the vibrations of, say, C_{2v} molecules do not span the point group and as they are also in relatively fixed positions, they could reasonably reduce relaxation rates. Fröhlich's then maintains this condition becomes significant when the field energy available in the system exceeds kT , which then could lead to collective motions at the lowest frequency, which would store energy in a coherent fashion, that is it could Bose condense.

We have analyzed a model system, which Fröhlich^[54] devised exactly as he proposed to see whether his example seemed consistent with other BEC systems. We begin (crudely) with a large number, Z , of units acting as a heat bath and capable of electric dipole oscillations with a certain frequency, ω_0 . Coulomb interaction between these oscillators gives rise to longitudinal electric modes in a narrow, but possibly shifted, modes in a frequency range $\omega_1 \leq \omega \leq \omega_2$. Letting ω_e be the frequency of an "enzyme" and ω_s , a "substrate"

$$\omega_{\pm}^2 = \frac{1}{2} (\omega_e^2 + \omega_s^2) \left[1 \pm (q^2 + Q^2)^{1/2} \right] \text{ where } q = \frac{\omega_e^2 - \omega_s^2}{\omega_e^2 + \omega_s^2}$$

Then, Q is the ratio of interaction energy of two giant dipoles (with correlated oscillations of elastically bound ions of charge e) to their potential energies which becomes

$$Q = \gamma e^2 (z_e z_s)^{1/2} / MR^3 (\omega_e^2 + \omega_s^2)$$

with γ , a constant (here taken as one). Nonlinear terms become essential and the attraction due to the giant dipoles

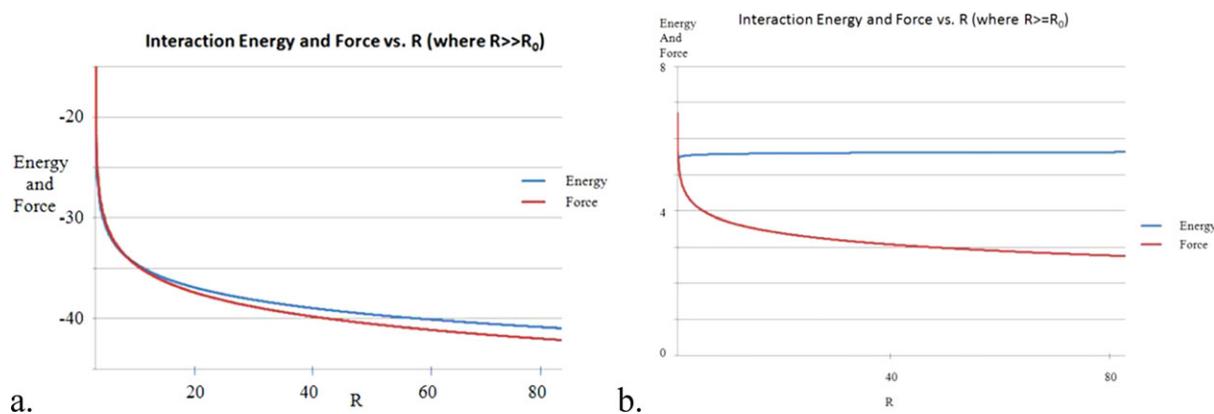


Figure 9. a) Plots of condition 1 (above) are shown for the interactions between two porphyrin molecules; it does not appear remarkable; rather, it is rather like a condition of $T \geq T_c$ (Fig. 3b). However, the condition 2 (Fig. 10b) where $R \approx R_0$ seems to show a slower algebraic decay than BKT vortices; it is possible that the system might exhibit coherence. But experiment is the real proof, especially in view of the comments in the text. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

becomes very large. The interaction energy I of the coupled oscillators can be expressed as the free energy difference at infinity minus the free energy at R , as expressed:

$$I = kT \log \frac{\omega_+ \omega_-}{\omega_s \omega_e} = \frac{1}{2} kT \log \left[1 - \frac{1}{4} \left(\frac{\omega_e}{\omega_s} + \frac{\omega_s}{\omega_e} \right)^2 Q^2 \right]$$

When $Q^2 \ll 1$, an attractive interaction proportional to $1/R^6$ holds (small though compared to kT); as the distance decreases, Q^2 becomes large and anharmonic and a transition to a highly polar metastable may be possible.

Setting (per Fröhlich) $\omega_e = \omega_s = \omega$, and $z_e = z_s = z$, the overall equations simplify to $\omega_{\pm}^2 = \omega^2(1 \pm Q)$ and interaction energy is

$$I = \frac{1}{2} kT \log(1 - Q^2) \text{ and } Q = \left(\frac{R_0}{R} \right)^3 \text{ while } R_0^3 = \frac{\gamma e^2 z}{M \omega^2} \quad (24)$$

There are two limiting conditions (Figs. 9a and 9b):

1 $R \gg R_0$ where $I = \frac{1}{2} kT \left(\frac{R_0}{R} \right)^6$ with the force (Casimir-like) between the two molecules. $f = -\frac{\partial I}{\partial R} = \frac{3kTR_0^6}{R^7}$

2 $R \approx R_0$; $I = \frac{1}{2} kT \log \frac{6(R-R_0)}{R_0}$ and $f = \frac{1}{2} \frac{kT}{R-R_0}$

Comparisons of these conditions are shown later for the interactions between two porphyrin molecules.

There has never been incontrovertible theoretical proof of exactly such a condition in a vibrational system (to the authors' knowledge), and there are several critical papers that further evaluate these ideas.^[55–57] Recently, Reimers and coauthors (R)^[56] have extensively examined the Fröhlich model, especially the work of Wu and Austin^[57] who derive a dynamic Hamiltonian that they suggested is the simplest model of a "Fröhlich condensate." R's analysis suggests three types of condensates: coherent, strong, and weak; their conclusion is that only a weak condensate in the microwave or terahertz region is feasible. They arrive at these results by an impressive analysis involving large numbers of input and bath oscillators, a uniform vibrational system. This is an ongoing discussion of the

Reimers study concerning their definition of excitation temperature and their source and bath coupling into one, a considerable constraint; an example of details can be found on "Nature network" blog, and so forth. Bolterauer et al.^[58–60] have also investigated the Wu–Austin Hamiltonian and found two interesting features: (1) perturbation theory cannot be used, as the nonlinear term not only does not converge but also has no lower bound, leading to the conclusion (2) that the ground state has no finite lower bound. They also raised the question as to whether Fröhlich's theory has a microscopic basis. It seems important to point out that during the search for a theory of superconductivity in the 1950s Feynman tried to solve the problem by infinite order perturbation theory summation on the Fröhlich electron–phonon interaction; the sum was zero. He did not succeed, because the energy gap related to the electron–phonon interaction is an essential singularity that cannot be solved by a power series,^[61] the details of which are in "Superconductivity Theory (BCS)" section. This issue might be similar for BEC as difficulty may arise with the delta function for the state accumulating population (see "Bose–Einstein Condensation (BEC)/Superfluid" section). In addition, one of us has performed a number of calculations on vibrational relaxation rates of excited electronic states (Squire and Jaffe, unpublished); the use of different coupled vibrational energies analysis changed the accessibility to portions of the vibrational relaxation subspaces. The addition of anharmonic terms and deuterium substitution for hydrogen also significantly altered the original rates; further, these effects have been experimentally verified by reducing the temperature and "freezing" the sample in a matrix or glass. Our conclusion was that there could be special systems where relaxation is dramatically reduced; to calculate these requires significant vibrational detail that might not be revealed by a sum of average oscillators. As pointed out by a referee, microtubules are thought to be favorable conditions for a Fröhlich condensate, presumably because dissipative vibrations can be restricted by symmetry.

The novelty of Fröhlich model is the recognition that the interaction (gigantic in some cases) of biological membranes can be described as harmonic oscillators and the possibility of BEC that might be strong in a special case, particularly if the metastable state is not optically active in a selection rule sense.

Recently, a BEC of magnons (a QP of a spin wave) at room temperature has been experimentally discovered^[62] and theoretically quantified.^[4] The condensate was formed by parallel pumping of Yttrium iron garnet (YIG) where the magnon–magnon relaxation time of a few nanoseconds is much shorter than the magnon–phonon relaxation of 1 μ s. The increase in magnon density raises the chemical potential, μ , and BEC begins when μ reaches the minimum magnon energy. Electronic systems that may display attributes of a Fröhlich model are considered in “Coherent Exciton Matter and Polaritons” and “Coherence in Photosynthesis” sections.

Resonance energy transfer

Experimental—fluorescence resonance energy transfer. The ability of modern spectroscopic equipment has resulted in a rebirth of fluorescence resonance energy transfer, as a particularly useful method of measuring distances of donor to acceptor energy transfer.^[63] A typical biochemical application can measure conformational change in a protein from a distance where no transfer was detected (calculated by other methods) to one which is calculated as 2 nm, Figure 10.

A Jablonski diagram (Fig. 11a) outlines the processes from left to right: absorption of energy ($S_0 \rightarrow S_1$), where the ground state absorbs a photon of energy (green line, far left) and populates an excited vibrational state of the first singlet excited state, S_1 ; yellow lines indicating radiationless transition to the lowest vibrational level of S_1 where fluorescent emission of light back to the ground state may occur, red solid line or energy transfer from the donor molecule to the acceptor molecule (dashed red line) with the blue arrow (the largest arrow in the figure) indicating the energy transfer process that occurs by virtual photon

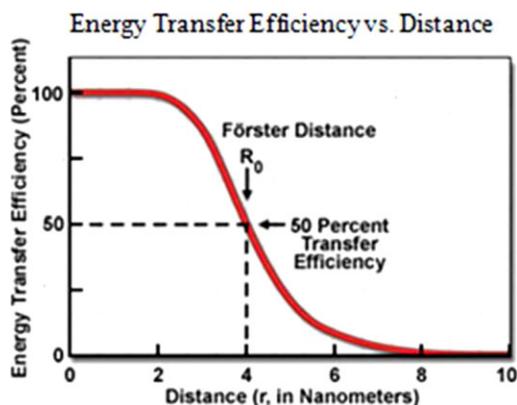


Figure 10. Illustration of distance and the transfer rate estimate. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

exchange from the donor to the acceptor. Then, the acceptor emits a photon of light that is detected, both in a temporal and spectral mode. Figure 11b illustrates calculation of the Förster radius, $R_0 = 50\%$ efficiency:

$$R_0 = \frac{c\kappa^2\phi_D}{n^4} \int d\omega f_D(\omega)\epsilon_A(\omega)\omega^4$$

where κ^2 is an orientation factor, c contains the dipole–dipole coulomb coupling (or higher moments, if necessary), ϕ_D is the lifetime of the donor excited state with no acceptor molecule nearby, n is the dielectric constant of the medium, and the integral accounts for the spectral overlap. The efficiency of the process is the ratio of photons collected from the donor and acceptor. The distance can then be calculated: $E(R) = \frac{1}{1+(R/R_0)^6}$.

Theory. The transfer process we are most interested in describing is the nontrivial long-range electronic (as opposed to vibrational) spin-conserved energy transfer from a “donor” to an “acceptor,” either by molecules or a “system,” to be yet defined.^[42,64,65] The short range, often called Dexter-type, consists of direct and exchange transfer, and operates over distances less than $10a_0$ (a_0 Bohr radius) where there is significant wave function overlap. Longer-range transfer, Förster-type, occurs over distances of $10a_0 < R < 100a_0$ and can be broken into three pieces,

$$E_{LR} = E_{\text{electrostat}} + E_{\text{induc}} + E_{\text{disp}}$$

the electrostatic, inductive, and dispersion terms, respectively. The weak and strong electronic couplings seem well understood and as Scholes notes, the Fermi Golden rule/perturbation theory seems established for these; we refer the reader to Förster, Scholes, and Salam for details and background. The intermediate coupling can lead to short timescale coherent dynamics and this seems to us to be the crux of the question of coherence in PS. Here, it seems unlikely a coherent system can be described by the Fermi golden rule approach as in principle, relaxation is to a continuum that is dissipative. The use of perturbation theory in this case may also be suspect. Further, London’s view of large molecules suggest that the dipole approximation must be abandoned for a long virtual oscillator and replaced by distinct poles, which more accurately reflect the physical extension of the oscillator. This view seems supported by the topology of the transition densities calculated by Krueger et al.,^[66] and it might lead to a collective effect; that is, not molecules acting individually through weak interactions, but stronger “system” dipoles acting together (coherently).

Coherent exciton matter and polaritons

The literature on polaritons has increased exponentially in the last 10 years, so it would be hopeless for us to cover the subject in any detail; this is to discuss the barest of essentials.^[67–69] An exciton can be formed from a material

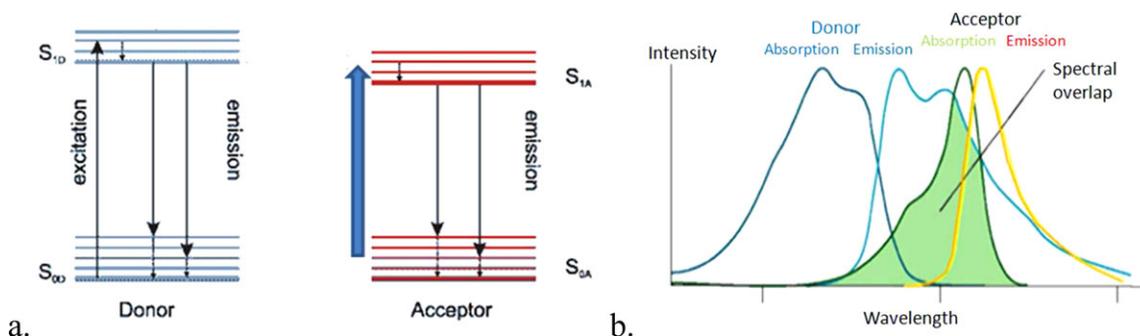


Figure 11. a) A Jablonski diagram is a convenient visualization of the many processes that may be active in a larger molecule. b) The spectral overlap as depicted contains electronic and vibrational (and possibly rotational?) energy contributions with multiple wave lengths. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

such as a semiconductor by absorbing a photon, creating an electron–hole dipole pair that will attract each other through a screened coulomb force.^[70] As there is screening (depending on the dielectric constant of the material), excitons be weakly bound (0.01 eV) in a large radius (a Wannier-Mott exciton) or more tightly bound (0.1–1 eV), a Frenkel exciton. An exciton can transport energy without charge transport; exciton transport carries no mass. A parabolic quantum well can be constructed of appropriate material by the binding of an optically excited electron with the hole created by an excitation process. Several wells can combine to form a two band system consisting of a valence band of holes and a conduction band of electrons.

A boson of small mass is created by the binding of excitons, and a BEC has been observed at low temperatures,^[71] interesting considering our earlier discussion about condensation that is not the ground state of the system. A single exciton wave function can be built from the Fourier transform of a hydrogenic wave function: $e^{\lambda} \sum_k \varphi_k a_{ck}^{\dagger} a_{vk} |0\rangle \Rightarrow [\sum_k \varphi_k a_{ck}^{\dagger} a_{vk}]^N |0\rangle$; the analogy with BCS Eq. (9) is clear:

$$|\Psi_{\text{BCS}}\rangle = \prod_{\mathbf{k}} \left(u_{\mathbf{k}}^* + v_{\mathbf{k}}^* \hat{\rho}_{\mathbf{k}}^{\dagger} \right) |0\rangle \quad |u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1$$

The same wave function can describe exciton BEC at low density and also the high density overlap of electron and hole Fermi liquids. This does not mean that they need to be coherent, but there is also a BCS-like instability of the Fermi surface. Experimentally, excitons can be trapped by stress-induced harmonic or optical traps, and they can have phase coherence with a macroscopic static dipole as an order parameter; theory suggests a dipolar superfluid might be possible. Excitons can directly decay into photons with the momentum of the electron–hole pair.

A polariton is a coherent mixture of an exciton and photon, created by adding light of the appropriate wavelength to couple with localized excitons in a microcavity. To describe this microcavity polariton interaction, we will use the Dicke Hamiltonian^[72] and follow Littlewood and others^[73–75]:

$$H = \sum_i \varepsilon_i \left(b_i^{\dagger} b_i - a_i^{\dagger} a_i \right) \quad \text{two-level system} \\ + \omega \psi^{\dagger} \omega \quad \text{photon} \\ g / \sqrt{N} \sum_{i=1 \dots N} \left(b_i^{\dagger} a_i \psi + \psi^{\dagger} a_i^{\dagger} b_i \right) \quad g(\text{coupling strength}) = d_{ab} \sqrt{2\pi \hbar \omega k}$$

Here, $a_i^{\dagger} a_i + b_i^{\dagger} b_i = 1$ and a_i creates a valence hole; b_i^{\dagger} creates a conduction electron, both on site i . The photon mode has $\lambda \gg a_{\text{Bohr}}$, the radius of the exciton, and couples to N excitons. Thus, there are two coupled order parameters, a coherent photon field $\langle \psi \rangle$ and an exciton condensate $\sum_i \langle a_i^{\dagger} b_i \rangle$. In this model, the excitation number consisting of excitons and photons is conserved $L = \psi^{\dagger} \psi + 1/2 \left(\sum_i (b_i^{\dagger} b_i - a_i^{\dagger} a_i) \right)$ and the BCS-like variational wave function is exact in the $N \rightarrow \infty$ limit with $L/N \sim \text{const.}$: $|\lambda, \mu, \nu\rangle = e^{\lambda \psi^{\dagger}} \prod_i (v_i b_i^{\dagger} + u_i a_i^{\dagger}) |0\rangle$ and

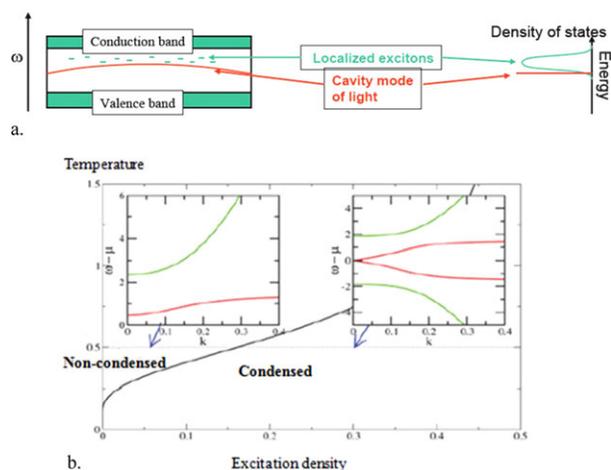


Figure 12. Two-dimensional model of a polariton in a microcavity. a) The band structure of quantum dot excitons (left) and localized excitons (right) coupling to an optical cavity light mode. b) An experimental signature of self-sustained coherence is indicated by the new branches in the excitation spectrum. (Reprinted with permission from J. Keeling, P. R. Eastham, M. H. Szymanska, P. B. Littlewood, Fig. 1, Phys. Rev. Lett. 2004, 93, 226403, © American Physical Society. <http://link.aps.org/doi/10.1103/PhysRevLett.93.226403>.) [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$u_i^2 + v_i^2 + 1$. But in a microcavity N does not go to infinity; so, there seems to be coherence and condensation, but not on a macroscale (similar to cold atom studies, "Ultracold Atomic gases and BEC" section). The summary of Figure 12 illustrates the experimental verification of coherence.^[78]

Figure 12b suggests the notion that decoherence is the adversary of coherence, not density where bosons can interact strongly. But even if a thermal distribution is obtained, the system can remain in nonequilibrium. Most of the decoherence is produced by particle flux, and as the number of excitons is not conserved, lifetimes are in the picosecond range. With the small exciton mass thus avoiding the mass limitation inherent in BCS and a number of other theories, see Eq. (7), the condensation temperatures could rise significantly, approaching room temperature and above. It should be noted that as one moves from coherence in electronic modes to coherence in optical modes there is a continuum from permanent excitonic condensates to standard lasers; the latter condition is lasing without inversion. A T_c of 19 K has recently been recorded for a polariton condensate.^[76]

Coherence in photosynthesis

A natural system Photosynthesis is the nearly 100% quantum efficient capture and transfer of solar energy to a reaction center where charge separation occurs (Fig. 13).^[77,78] Photon absorption takes place in the light harvesting antenna, followed by exciton annihilation at the reaction center. The efficiency of this process is enabled by an accompanying protein structure that orients and holds the antenna pigments at optimal positions.^[79] Recently, wave-like energy transfer^[80] and exciton quantum coherence has been detected in these complexes at physiological temperatures^[81] using the Fenna-Matthews-Olson (FMO) antenna complex (Fig. 14). The FMO complex is very specifically designed with the supporting structure resulting in an arrangement of molecules with approximate C_3 symmetry; the three BChl *a* subunits (trimers) are related to each other by a 120° rotation.^[78] One subunit containing seven BChl *a* structures is illustrated and numbered

in Figure 14a along with the energies and what is believed to be the two energy excitation transfer paths, beginning with BChl 1 and BChl 6, Figure 14b.

An interesting experimental feature is that both energy paths flow to BChl 3, a common low energy point for energy transfer to the reaction center which may use BChl 4 for storage. Spectroscopic hole burning and the resulting effects^[82,83] offer a good diagnostic tool to provide information on diagonal energy disorder, heterogeneity and linear electron-phonon coupling. Results and conclusions are as follows: the subunit dipole-dipole matrix elements, which vary from 10 to 200 cm^{-1} ; the trimer interaction is estimated to be about 20 cm^{-1} ; the diagonal disorder energy is estimated to be large, so it and the excitonic interactions are equally important. Further, BChl *a* molecules in the subunits are not suitable for "dark" intermolecular charge-transfer states; and Forster theory cannot account for ultrafast energy transfer decays and is also not applicable for the low temperature features that continue to higher temperature. The hole burning spectral distortions cannot be explained by linear electron-phonon coupling. The FMO complex is a strongly exciton-coupled system; following Small, the factor group C_3 separates the 21 states into 7 totally symmetric (A asymmetry) and the remaining 14 doubly degenerate E states; the former are polarized along the C_3 axis, while the latter are polarized perpendicular to it. The optical properties have been recently summarized.^[84]

The protein environment appears constant from 77 to 277 K, and efficient quantum transport is a balance between unitary (oscillatory) and dissipative (dephasing) dynamics that seems to be optimized at room temperature, enhancing the process robustness.^[81] Additionally, others have independently verified that this interplay between dephasing and quantum coherence results in highly efficient electronic energy transfer that is fast and unidirectional.^[85,86] Assuming initial coherence between two excitons $\Psi(t) = c_1\phi_1 + c_2\phi_2$, the density matrix time evolution is

$$\Psi(t) = c_1|\phi_1\rangle\langle\phi_1| + c_2|\phi_2\rangle\langle\phi_2| + c_1c_2^*e^{-i(E_1-E_2)t/\hbar}|\phi_1\rangle\langle\phi_2| + c_1^*c_2e^{-i(E_1-E_2)t/\hbar}|\phi_2\rangle\langle\phi_1| \quad (14)$$

The exciton populations are represented by the first two terms and the remaining two term describe possible coherences which when experimentally resolved, can result in quantum "beats," the frequency of which is due to energy differences between two excitons, $\nu = E_2 - E_1/\hbar$. Coherence among excited states exceeds 660 fs demonstrating that it is stronger than the ground state (70 fs). A summary and commentary of theoretical models used to calculate coherence in these systems^[87-90] has been presented by Wolynes.^[91] The general idea is that if a system demonstrates quantum coherence, it samples many paths (quantum trajectories) through the maze of a biological system to find the most efficient one. Wolynes compares protein motions to the motion of a clock; the motions of low frequency rapidly lose coherence, whereas higher frequencies are repetitive and consistent.

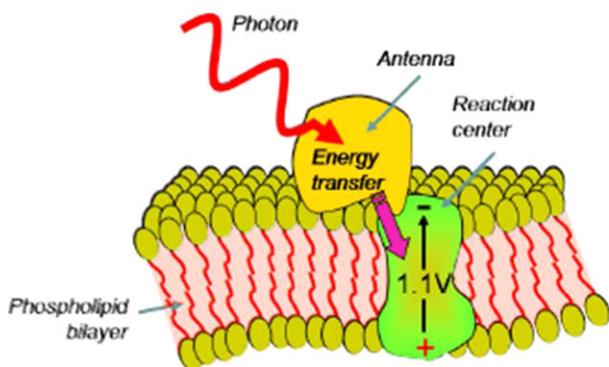


Figure 13. A crude depiction of the structures involved in photosynthesis. There are a wide variety of antenna structures, but most reaction centers are similar. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

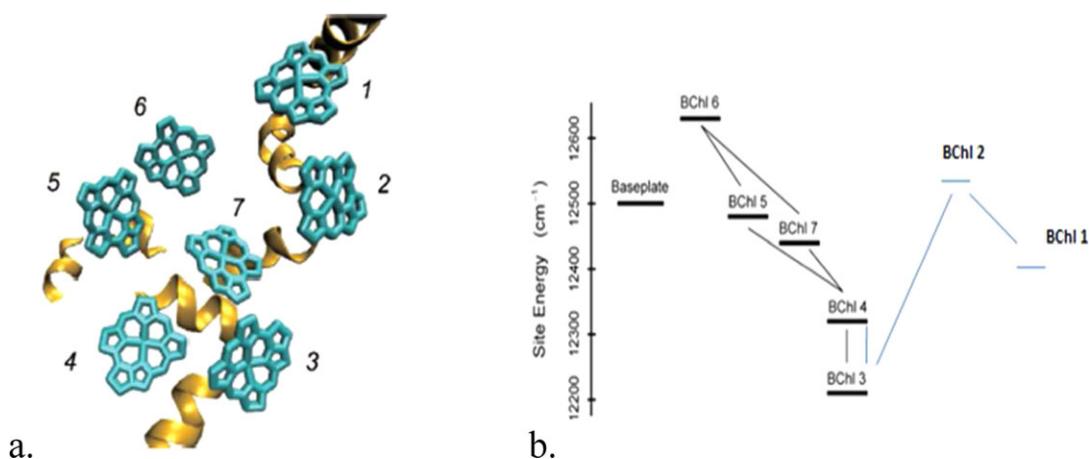


Figure 14. a) Seven BChl *a* structures in one of three subunits of the FMO complex, rigidly oriented by α helices. b) Two excitation paths beginning with BChl 1 and BChl 6; both terminate at BChl 3 (after Refs. [77,78]). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Our description of the FMO complex uses the coherence attributes in Part 1. The description of the interacting BChl *a*'s as a molecular dipole has to be abandoned as London suggested and instead described in an exciton basis where the exciton can be comprised as a charge separation residing on two or more molecules; there might even be mini positive and negative bands as illustrated in Figure 12a. A coherent system, Eq. (14), would then contain several more terms; as all of the energies are almost identical, an approximate single eigenvalue of the density matrix results. The system most likely will be a spontaneous emergent coherent system and thus contain Penrose's ODLRO ("Bose Einstein Condensation (BEC)/Superfluid" section) where a photon excitation can be annihilated at a point \vec{r} , absorbed into the condensate and a second particle can be created at an arbitrary distance \vec{r}' out of the condensate, with finite amplitude and no dissipation. The rate of this process would overwhelm the energy flow to the reaction center where it could be damaged, so dephasing is a regulator mechanism, as others have suggested, induced by a second coherent system, the regulator. The logical position for the regulator would be to stop energy flow to two nearly degenerate states (827 and 824 nm), attributed by Small to be the result of diagonal disorder, but which may also be lowered in energy by a Cooper-like interaction ("Superconductivity Theory (BCS)" section). Cooper's result, illustrated for a three body model, would give two states at energy 2ε and the third state at $2\varepsilon - 3V$ with a Schrieffer-type wave function:

$$|\Psi\rangle = \frac{1}{\sqrt{3}}[|1_k, 0, 0\rangle + |0, 1_k, 0\rangle + |0, 0, 1_k\rangle]$$

The excitons are highly correlated in a 1:1:1 mix of the three states. So energy flows until the reaction center becomes the bottleneck; the two nearly degenerate states (and possibly several others) store energy and stop energy flow in an out of phase mode while waiting on the reaction center to complete the charge separation. After the photon is released from the lowered state, the regulator system becomes coherent again with the other coherent antenna BChl *a* and energy-transfer

resumes; significant protection of the system and improved efficiency in energy transfer would result.

The coherence/decoherence could also have a component of Josephson's theory. Assuming the model earlier, when the regulatory portion was occupied by a photon, the induced phase difference $\Delta\phi$ between the antennae and regulators would generate a potential difference V as expressed by Eq. (14). Josephson theory then leads to a periodically variation with frequency $2eV/\hbar$ which would not be unreasonable when compared to the experimental beating frequency of 160 cm^{-1} . Indeed, this might imply there could be other coherence component triggers such as the presence of a photon field (polariton); it would be interesting to experimentally test a photon effect and other variables from Josephson junction experiments. It is recognized that experiment is the final proof.

Discussion, Conclusion, and Comments, Unanswered Questions

Discussion

The beginning of this review sought to unify the concepts of:

- Coherent macroscopic occupation of a single state (inherently bosons or fermions paired in such a manner that they behave as bosons).
- Criteria for BEC condensation of the particles in the macroscopic occupation that results in.
- A state where the phase θ becomes "locked" at a common value between the constituent particles occupying the state which "breaks" electromagnetic symmetry $e^{i\theta}$ creates a collective degree of freedom of the particles.

Systems that have these attributes have a number of fascinating properties, and there are some systems that may be "borderline" in some of these attributes, which still contain some of these properties.

A BEC in an ideal boson gas results in a thermodynamic phase transition. Hence, the concept of SEC is a broadening of the BEC concept, which does not require a phase transition. It is useful for several reasons: a traditional laser does not have a

Table 3. Possible Types of Coherence.

Section	Type	Particle (P) Quasiparticle (QP)	Lifetime	Phase transition	Spontaneous emerg coherence	Comments
3	BEC/SF	Boson	Depends on conditions	Yes	Yes	Spontaneous coherence essential; symmetry breaking
4	BCS	Cooper pairs (Quasiboson)		Yes (BEC)	Yes	Symmetry breaking
2	Laser	Photon	Variable	No	Yes	Symmetry breaking
5	Cold atomic gases	Fermions and bosons	Depends on conditions	Yes	Yes	BEC in trap; not thermodynamic limit
6	Casimir effect	Photon exchange	Uncertainty principle	No	No	
7	Fröhlich	Magnon/exciton?	Nanosecond	Yes?	Yes?	
8	Forster (FRET)	Single irreversible photon exchange	Nanosecond	No	Doubtful	Strong (exchange) and weak (pert theory) understood; intermediate— incoherent and irreversible
9	Exciton	Exciton (Quasiboson)	Picosecond	Yes	Yes	Verified experimentally
	Polariton	Exciton photon condensate	Picosecond	Yes	Yes	Verified; two different bosons coherently condensing
10	Photosynthesis	Exciton or polariton condensate?	Picosecond	?	Yes	Experimental coherence (quantum beats); complicated structures and multiple estimated interaction strengths

phase transition (lasing in a micro cavity does^[92]); or a QP may develop incipient coherence with other QPs, but the lifetime of the QP may not be long enough to allow measurement or allow the development of a full-fledged phase change. It seems that a fluctuational coherence in a mesoscopic system may not undergo a phase change (photosynthesis), but it seems that it can have several segments, which exhibit interferences and this could be considered as a suitable working definition of SEC. If this be the case, photosynthesis could be a prototype for microenergy transfer, which is exhibited in many biological systems. There are several systems discussed in part 2 of this review that may have SEC; experimental evidence is the deciding factor.

Conclusions and unanswered questions

1. Per London, oscillators with an inherent multipole can polarize each other leading to interesting physical effects. Quantization leads to virtual boson exchange in most cases. Some exchanges are quite fast, whereas others are slower (retarded). The Casimir effect seems to have aspects of both, where the larger distance requires taking the speed of light into consideration.

2. Several phenomena discussed have the common feature that virtual boson exchange is crucial, either between true bosons or composite boson whose constituents are fermions that obey the Pauli principle. Some of these systems have a form of coherence; others do not as a result of the interaction details. Is the difference between SEC that has symmetry breaking via ODLRO and “true” BEC resulting in a phase change only dependent on the conditions, that is, the laser in “The Laser/Maser” section versus Ref. [92]? Can a system be forced from one extreme to the other? Could this be a continuous migration?

3 Several of the systems discussed have overt macroscopic effects, such BEC, superconductivity, and the Casimir effect.

Others seem to have only microscopic or mesoscopic effects such as Förster resonance transfer. It seems that if these smaller systems have true coherence, they might be described by a large eigenvalue in the “local” density matrix.

4 While it seems that relaxation effects are important, the degree to which they enter seems variable. If they were somehow controllable, so they could be “frozen out,” could the microcoherence systems become macro?

5 It would be interesting to know if the methods used to calculate coherence^[91] could derive a BEC or superconducting macroscopic coherent system.

6 Elaboration on the exciton/polariton possibility in a more quantitative manner would offer a more thorough comparison to photosynthesis to answer which mechanism, if either, might be operative.

Acknowledgments

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APPENDIX A: QUASI PARTICLES

A QP is a description of a complex interacting system that behaves as if it were composed of weakly interacting particles in free space. The term/concept originated with Landau’s Fermi liquid theory (FLT),^[10] which offers a good description of a metal with interacting electrons. A key tenet is a one-to-one relationship between excited states of a normal metal and a noninteracting electron gas. Elementary excitations in FLT are QPs, a composite particle with a lifetime that depends on collisions with other QPs. A QP of energy $\varepsilon_{\vec{p}}$ with an infinite lifetime τ is an eigenstate of the system with the condition $\hbar/\tau \ll \varepsilon_{\vec{p}}$. As $\varepsilon_{\vec{p}} \rightarrow \varepsilon_F$, the lifetime $\tau \rightarrow \infty$ and the QP is stable

at the Fermi level. A second key point is that the electron mass is significantly renormalized. The scattering rate of electrons in the vicinity of the Fermi level can be shown to vanish as $(\varepsilon_1 - \varepsilon_F)^2$, where ε_1 is the energy of an electron above the Fermi surface. Phillips has details.^[89,95]

APPENDIX B: COHERENCE AND THE DENSITY MATRIX FORMALISM

The density matrix provides a technique to account for coherent/incoherent populations. The density operator is $\rho = |\psi\rangle\langle\psi|$, and for our purposes a matrix operating on a complete set of states whose elements are $\langle\psi_n|\rho|\psi_m\rangle$, and substituting,

$$\rho_{mn} = \langle\psi_n|\rho|\psi_m\rangle = \langle\psi_n|\psi\rangle\langle\psi|\psi_m\rangle = c_m^*c_n$$

with probability amplitudes c_m and c_n for occupation of the states. The diagonal elements of the density matrix is normalized to one, because an individual state is occupied,

$$\text{Tr}\rho = \sum_n \rho_{nn} = \sum_n |c_n|^2 = 1$$

This enables us to determine if a system is in a pure quantum state or a mixed state, a random ensemble of pure states. In a pure state that might be a linear superposition of different states, the uncertainty is intrinsic in quantum mechanics. Nonetheless, we can change the basis and formulate a different description of the state through a basis change; the result would be the amplitude and phase of a single quantum state as we have described for BEC (either genuine bosons or such as Cooper pairs or excitons):

$$\psi(\vec{r}, t) = \sqrt{n_0(\vec{r}, t)}e^{iS(\vec{r}, t)}$$

We call this state coherent and such a state usually arises from a thermodynamic phase change. In a mixed state, this is not the case; the randomness is due to statistical uncertainty. The statistics of the particles play an important role; boson coherence has been well defined. Coherence between fermions seems to lead into discussions of Grassman variables (on which we defer discussion) and electron correlation. The Lowdin definition^[93] of electron correlation (the exact energy minus the Hartree-Fock energy) has been questioned recently^[94] as more sophisticated calculation methods are brought to bear on the problem. Following Glauber, we can describe the various correlation functions as consequences of a single inequality that he proves, p. 18^[8]:

$$\text{Tr}\{\rho A^\dagger A\} > 0$$

which holds for the operator A of arbitrary choice. As the trace is invariant and various correlation functions essentially have the same basic structure, only the choice of the A choice is different. For example, a beginning is an optical experiment where we superimpose two beams (fields) and generate inten-

sity fringes (Young's type experiment). Coherence here is measured by intensities which quadratic in field strengths. With the advent of nonlinear optics, coherence needs to be more precisely as devices that generate the fourth and higher powers of field strength at much longer ranges cannot be fully characterized. (See section 9.7, p. 366 of Ref. [8] for examples.) An example in the spirit of this study would be the two other seemingly different types of coherency frequently discussed in the literature that are experimentally accessible should be described using Glauber's relationship; they are:

1. A coherent, extended wave function of an electron or QP that can be scattered causing decoherence.

2. An NMR view of an isolated ensemble of oscillators perturbed by a classical wave causing the oscillators to be "not exactly identical" resulting in decoherence.

With the discussion in mind in this section the question of 'electron correlation' seems ambiguous to some of the authors.

Keywords: emergent coherence · BEC · energy transfer

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