Exact Upper Bound on Barrier Penetration Probabilities in Many-Body Systems: Application to "Cold Fusion"

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The rate of tunneling of nuclei to classically forbidden small relative separation, in a fully interacting quantum-mechanical many-body system in equilibrium, is rigorously bounded above by a value calculable in terms of the Born-Oppenheimer potential between the nuclei. In the "cold-fusion" problem, the bound can be related to the affinities of helium and deuterium atoms to the metal in question, and shows that the allowed rate of tunneling of deuterons is far too small to be consistent with inferred rates of fusion.

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Two recent experiments have claimed evidence for a surprisingly high rate of the nuclear fusion reaction $d+d \rightarrow {}^3\mathrm{He}+n$ in deuterium trapped in palladium[1,2] and titanium.[2] Possible intrinsic sources of enhancement of the fusion rate include a large suppression of the Coulomb barrier between deuterons arising from many-body screening effects, an unusual enhancement of the nuclear reaction rate produced by the solid-state environment, or an exotic mechanism relying on coherence between fusion processes involving different deuteron pairs. We focus in this Letter on the first possibility. In the absence of the latter two mechanisms, the rate of fusion in a system containing N deuterons is $RN/2$, where $R=AP(0)$, A is the total intrinsic reaction rate for the processes $d+d \rightarrow {}^3\mathrm{He}+n, {}^3\mathrm{H}+p$ at zero relative separation, $\mathbf{r}=\mathbf{r}_i-\mathbf{r}_j$, and $P(0)$, the object of our study, is the probability density of finding two deuterons at $\mathbf{r}=0$, averaged over the motion of their center of mass, the other $N-2$ deuterons, and the remainder of the solid-state environment. Since[3] A is $\sim 1.5\times 10^{-16}$ cm^3/sec, to obtain the value of R ($\sim 10^{-23}$/sec) quoted in Ref. 2 (and *a fortiori* that inferred in Ref. 1) requires that $P(0)$ be at least $\sim 10^{-7}$/cm^3.

A naive estimate using the wave function for relative motion in a repulsive Coulomb potential at energies ~ 1 eV in a classically accessible volume ~ 1 Å^3 gives $P(0) \sim 10^{-300}$/cm^3. The crucial question is whether a sophisticated many-body screening effect in metals could lead to an enhancement of the magnitude required. Since the rate depends exponentially on parameters such as the classical distance of closest approach of the deuterons, the required enhancement is not necessarily implausible. Recently we showed[4] that within the lowest-order Born-Oppenheimer (BO) approximation no such enhancement is possible in a metal in equilibrium, given essentially known facts about the behavior of ^{4}He in these metals. However, that argument does not answer the question completely. In the first place, even if the screening were entirely due to the electrons of the metal, the fact that the expansion parameter m/M_d (where m is the electron mass, and M_d is the deuteron mass) of the BO expansion is small, $\sim 5\times 10^{-4}$, does not guarantee that corrections of high order in m/M_d are unimportant in calculating exponentially small probabilities; the more so in a metal, as distinct from say the D_2 molecule, because the electronic excitation energies can be arbitrarily small. Second, the effects on the tunneling of a particular deuteron pair of the motion of "third-party" deuterons, let alone that of the nuclei of the metal itself, are not at all well described by the lowest-order BO approximation. Koonin has recently suggested[5] that such fluctuations could lead to a substantial enhancement of the barrier penetration probability.

In this Letter we obtain an *exact upper limit*, within the framework of nonrelativistic quantum mechanics, on the tunneling of two deuterons to the origin $\mathbf{r}=0$ of their relative coordinate. This limit is expressed in terms of the energy E of the many-body state in question and the affinities of deuterium and helium to the metal; the bound makes no assumptions whatever about the nature of any many-body mechanism involved, nor does it depend on the validity of the Born-Oppenheimer approximation. In the case of two isolated deuterons at temperature $T=0$, the limit rigorously implies that $P(0)$ cannot exceed 2×10^{-31}/cm^3 and thus that *R is bounded above by a rate* $\sim 3\times 10^{-47}$/sec, a value over 23 orders of magnitude below that reported in Ref. 2. For the case of many deuterons at $T=0$ our result shows that the necessary enhancement cannot be achieved without a totally incredible value of the deuteron pair correlation function at atomic separation; in thermal equilibrium at room temperature such enhancement would require at a minimum very exotic long-range influences on the tunneling process. Although proved for equilibrium, the argument also strongly constrains any nonequilibrium enhancement mechanism, by limiting the enhancement in the equilibrium base-line theory on which such a mechanism might be constructed.

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The argument proceeds in three stages. We first prove the quite general result that the exact rate of tunneling of a pair of nuclei into the classically forbidden region, in a condensed-matter system, is bounded above by the rate calculated for any spherically symmetric lower bound on the lower-order BO potential, $U(\mathbf{r})$ (defined precisely below), for the motion of the relative coordinate $\mathbf{r}$ of the pair. Specifically, suppose that $U(\mathbf{r})$ is bounded below by some spherically symmetric potential $V_2(r)$ (where $r=|\mathbf{r}|$). For a given energy E of the many-body state, we define $r_0(E)$ as the largest distance for which $V_2(r)-E\geq 0$ for all $r\leq r_0(E)$. We define $\rho(r)$ as the probability density angular averaged in $\mathbf{r}$; $B(\mu,r,E)$ as $\ln[\rho(r)/\rho(0)]$, where μ is the reduced mass of the pair; and $B_0(\mu,r,E)$ as the value of B calculated for the one-body problem with potential $V_2(r)$. Then for any $r\leq r_0(E)$ we have the general inequality

$$B(\mu,r,E)\geq B_0(\mu,r,E)\,. \tag{1}$$

In the second stage we use an improved version of the argument of Ref. 4 to make a judicious choice of $V_2(r)$, and in the third stage exploit these results to obtain upper limits on $P(0)$.

State I.—In the proof of (1) we collectively denote by ξ all the coordinates of the many-body system except the relative coordinate $\mathbf{r}$ of the deuteron pair in question. We reserve the notation ∇ for gradients with respect to $\mathbf{r}$, and write $\int d\xi$ as a shorthand for the many-dimensional integration over ξ. Note that ξ includes not only all electron coordinates, but also the center-of-mass coordinate of the deuteron pair, and all coordinates of "third-party" deuterons and of the nuclei of the metal.

The Schrödinger equation for a stationary-state wave function $\psi(\mathbf{r},\xi)$ of the many-body system may be written as

$$\left[-\frac{\hbar^2}{2\mu}\nabla^2+\hat{H}(\mathbf{r})\right]\psi(\mathbf{r},\xi)=E\psi(\mathbf{r},\xi)\,. \tag{2}$$

The operator $\hat{H}$ is a function of the coordinates ξ and their conjugate momenta, and depends on $\mathbf{r}$ through the interaction of the two deuterons with each other and with the rest of the system. The lowest eigenvalue, $U(\mathbf{r})$, of $\hat{H}(\mathbf{r})$ at a given $\mathbf{r}$ is the potential for relative motion in the lowest BO approximation. (It should be carefully noted that since the latter is defined by letting *all* other coordinates, including the "slow" ones, adjust to the instantaneous value of $\mathbf{r}$, this potential may differ somewhat from the one derived in the approximation in which all the nuclei are held fixed.) Since $U(\mathbf{r})$ minimizes the expectation value of $\hat{H}(\mathbf{r})$ for a given normalization of the wave function over ξ, we can write

$$\int d\xi\,\psi^*(\mathbf{r},\xi)\hat{H}(\mathbf{r})\psi(\mathbf{r},\xi)\geq U(\mathbf{r})\int d\xi\,|\psi(\mathbf{r},\xi)|^2 \equiv U(\mathbf{r})\rho(\mathbf{r})\,, \tag{3}$$

where $\rho(\mathbf{r})$ is the total probability density to find the deuterons at $\mathbf{r}$; hence from (2) we have

$$\frac{\hbar^2}{2\mu}\int d\xi\,\psi^*(\mathbf{r},\xi)\nabla^2\psi(\mathbf{r},\xi)\geq[U(\mathbf{r})-E]\rho(\mathbf{r})\,. \tag{4}$$

By using the Schwarz inequality, and the fact that differentiation with respect to $\mathbf{r}$ commutes with integration over ξ, one may show[6] that for any real wave function f [here $|\psi(\mathbf{r},\xi)|$] one has $\int d\xi f\nabla^2 f\leq g\nabla^2 g$, where $g^2\equiv\int d\xi f^2$. Thus from (4) we obtain

$$\frac{\hbar^2}{2\mu}\frac{\nabla^2\chi(\mathbf{r})}{\chi(\mathbf{r})}\geq U(\mathbf{r})-E\,, \tag{5}$$

where now $\chi(\mathbf{r})\equiv\rho(\mathbf{r})^{1/2}$. We may formally regard the quantity $\chi(\mathbf{r})$ as the solution of the Schrödinger equation for a particle of mass μ moving in a potential $V_1(\mathbf{r})\equiv(\hbar^2/2\mu)[\nabla^2\chi(\mathbf{r})]/\chi(\mathbf{r})+E$. Then if $V_2(r)$ is any direction-independent lower bound on $U(\mathbf{r})$, we have $V_1(\mathbf{r})\geq V_2(r)$.

Let us define $\phi(r)$ to be the solution of Schrödinger's equation that is regular at the origin, for a particle of mass μ in the potential $V_2(r)$, at energy E. Then since both $\chi(\mathbf{r})$ and $\phi(r)$ can be taken to be positive, finite, and continuous for all $r\leq r_0(E)$, where $r_0(E)$, as above, is the classical turning point in the potential $V_2(r)$, a simple application of Green's theorem to the quantity $\chi\nabla\phi-\phi\nabla\chi$ gives the result that as r decreases, $\ln\chi(r)$ decreases faster than $\ln\phi(r)$ for all $r\leq r_0(E)$, where, as above, $\chi(r)$ denotes the angular average of $\chi(\mathbf{r})$. Noting that B_0 is defined in terms of ϕ^2, we immediately derive the inequality (1).

State II.—We now obtain a suitable potential $V_2(r)$ for constructing a useful bound on the tunneling rate. We write the quantity $\hat{H}'(\mathbf{r})\equiv\hat{H}(\mathbf{r})-e^2/r$ in the form

$$\hat{H}'(\mathbf{r})=-\frac{\hbar^2}{2M_4}\nabla_R^2+[V_c(\mathbf{R}+\mathbf{r}/2;\bar{\xi}) +V_c(\mathbf{R}-\mathbf{r}/2;\bar{\xi})]+\hat{K}(\bar{\xi})\,, \tag{6}$$

where $\mathbf{R}$ denotes the center-of-mass coordinate of the deuteron pair; $\bar{\xi}$ denotes all coordinates of the environment, other than $\mathbf{R}$ and $\mathbf{r}$; $V_c(\mathbf{a})$ is the Coulomb interaction between a deuteron at point $\mathbf{a}$ and the environment; and $M_4=2M_d$ is the mass of the α particle (up to the nuclear binding energy, which is irrelevant here). We let $\psi_0(\mathbf{R},\bar{\xi};\mathbf{r})$ be the lowest eigenfunction of $\hat{H}'(\mathbf{r})$, for fixed $\mathbf{r}$, with corresponding eigenvalue $E'(\mathbf{r})$. Then choosing, for the state $\psi_0(\mathbf{R},\bar{\xi},0)$, a trial density matrix that is a mixture of $\psi_0(\mathbf{R}+\mathbf{r}/2,\bar{\xi};\mathbf{r})$ and $\psi_0(\mathbf{R}-\mathbf{r}/2,\bar{\xi};\mathbf{r})$ with equal weights, one easily demonstrates[7] $E'(\mathbf{r})\geq E'(0)$. But $-E'(0)$ is by definition the binding energy of an α particle in the metal.[8] Thus using the fact that the ground-state energy relative to that without the two deuterons cannot be greater than (minus) twice the binding energy of a single deuteron to the metal, and measuring all energies from the many-body ground state with the two deuterons present, we may write a lower limit

$V_2(r)-E$ on $U(\mathbf{r})-E$ as

$$V_2(r)-E=\frac{e^2}{r}-\lambda(E)\frac{e^2}{a_0}, \tag{7}$$

where $\lambda(E)\equiv\lambda_0+E/(e^2/a_0)$; here

$$\lambda_0=E_4+K_4-2(E_d+K_d). \tag{8}$$

The experimentally observable energies on the right-hand side, all measured in hartrees (e^2/a_0), are, in order, the binding energy of the ^{4}He atom, the affinity of ^{4}He to the metal in question, the binding energy of a deuterium atom in free space, and its affinity to the metal. (Note that unlike in Ref. 4, the zero-point energy of the α particle does not enter this form of the argument.)

The deuterium affinity, K_d, is[9] 0.087 hartree in Pd and presumably of similar size in Ti; to the best of our knowledge there is no published direct measurement of the helium-atom affinity, K_4, for Pd or Ti, but the fact that at room temperature ^{3}He desorbs[10] from Ti and forms bubbles[11] in Pd suggests that, as for other metals, K_4 is either positive or very small ($\ll 1$ eV). A conservative estimate is therefore $\lambda_0\simeq 1.78$. [Strictly speaking, K_4 and K_d should be evaluated in the actual (deuterium-soaked) ground state, but since it would take a quite extraordinary and unprecedented dependence on deuterium concentration, c, to affect the results appreciably, we use $c=0$ values. Any corrections are easily incorporated.]

Stage III.—We write the inequality (1) in the form $\rho(r)/\rho(0)\geq\phi^2(r)/\phi^2(0)$, where $\phi(r)$ is defined as in stage I, and integrate both sides over a sphere of radius $r_0(E)$. Introducing the standard notation for the Coulomb problem,[12]

$$z\equiv\frac{2\eta(E)}{r_0(E)}r,\quad \eta(E)\equiv\left(\frac{M_d}{4m\lambda(E)}\right)^{1/2} \tag{9}$$

(z is the variable ρ in Ref. 12, a notation we avoid for obvious reasons), we obtain the inequality

$$\rho(0;E)\leq\frac{1}{4\pi}\left(\frac{2\eta}{r_0}\right)^3\int_{r\leq r_0}\rho(\mathbf{r})d^3r\left[\frac{[F_0'(0)]^2}{\int_0^{2\eta}F_0^2(z)dz}\right], \tag{10}$$

where $F_0(\eta,z)$ is the $L=0$ radial Coulomb wave function (Ref. 12, Sec. 14.1). Noting that $F_0''(z)\geq 0$ for z less than the turning point 2η, and $F_0(0)=0$, we readily see that a lower bound on the integral in the denominator is $F_0^3(2\eta)/3F_0'(2\eta)$. Using the explicit formulas (14.6.2), (14.1.8), (14.5.10), and (14.5.11) of Ref. 10, we can write the result in the form

$$\rho(0;E)\leq\left(\frac{3}{4\pi r_0^3(E)}\int_{r\leq r_0}\rho(\mathbf{r})d^3r\right)\times Q(E)\eta^{10/3}(E)e^{-2\pi\eta(E)}, \tag{11}$$

where $Q(E)$ is the number which depends weakly on E, and for $E=0$, $\lambda_0\simeq 1.78$, is approximately 60.

For a single pair of deuterons, for which $P(0)\equiv\rho(0;E)$, the integral in Eq. (11) is clearly bounded above by unity. Then, putting in the numbers, we find that at zero temperature *the equilibrium value of P(0) for dd fusion cannot exceed* $2\times10^{-31}/\mathrm{cm}^3$. Similar evaluations lead, for the reaction $p+d\rightarrow{}^3\mathrm{He}+\gamma$, to an upper bound on $P(0)$ of $3\times10^{-20}/\mathrm{cm}^3$, and a reaction rate $R_{pd}\leq10^{-41}$/sec; and for the reaction $d+t\rightarrow{}^4\mathrm{He}+n$, to $P(0)\leq4\times10^{-37}/\mathrm{cm}^3$, and $R_{dt}\leq10^{-50}$/sec. We reemphasize that these results are exact, to within small numerical uncertainties arising from the poorly known value of K_4 and its variation (and that of K_d, etc.), with hydrogenic concentration.

In the physically more relevant case of N deuterons, we define the dimensionless correlation function

$$G(\mathbf{r};E)\equiv(N\rho_0)^{-1}\sum_{ij}\rho(\mathbf{r}_{ij};E)_{\mathbf{r}_{ij}=\mathbf{r}},$$

where ρ_0 is the average deuteron density. Then if we sum the inequality (11) (which applies to an arbitrary pair ij) over i and j, and let $\bar{G}(E)$ denote the average of G over the sphere $r\leq r_0(E)$, we find an upper limit on

$$P(0)\equiv N^{-1}\sum_{i,j}\rho(\mathbf{r}_{ij})_{\mathbf{r}_{ij}=0}$$

to be

$$P(0)\leq\rho_0\bar{G}(E)Q(E)\eta^{10/3}(E)e^{-2\pi\eta(E)}. \tag{12}$$

Estimating the maximum deuterium concentration as two per metal ion, we find that at zero temperature $P(0)\leq4\times10^{-33}\ \bar{G}/\mathrm{cm}^3$, where $\bar{G}$ is the dimensionless correlation function averaged over the *classically forbidden* region of relative motion. To obtain a value of $P(0)\geq10^{-7}/\mathrm{cm}^3$ requires the total incredible value $\bar{G}>10^{25}$. (Such a value would *inter alia* imply partial Coulomb interaction energies well beyond TeV per deuteron, and could very likely be rigorously refuted by an argument similar to that of state II above, but we shall not do this here.)

The case of finite temperature is slightly trickier, since in order to get rigorous results we have to take E to be the total energy of the many-body state measured from the ground state, a quantity proportional to the total number of particles in the system. It is clear from (9), (11), and the definition of $\lambda(E)$, that for two isolated deuterons, to obtain a value of $P(0;E)$ of the order of $10^{-7}/\mathrm{cm}^3$ requires at least an energy of the order of 80 eV [and a similar number for the many-deuteron case as long as $\bar{G}(E)$ is not highly anomalous].[13] If we use a microcanonical ensemble and take into account that the thermal energy per atom at room temperature of Pd (and D) is of order the Dulong-Petit value (0.075 eV), we see that such an energy value cannot be achieved at room temperature in an assembly of fewer than ~1000 atoms. Correspondingly, in a macroscopic system at

least this number of atoms would have to collaborate to achieve the required enhancement. While we have not been able rigorously to rule out such an exotic long-range effect operative only at finite temperature, it seems extraordinarily implausible.

We conclude that if the "cold fusion" claimed[1,2] to have been observed in D trapped in Pd and Ti is a real phenomenon, it is unlikely in the extreme to be due to solid-state enhancement of equilibrium probabilities. Our argument clearly can also be used to put severe constraints on the efficacy of nonequilibrium mechanisms, once these are specified in detail.

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