extinction episodes occurred at 11.3, 38, 65, 91, 125, 144, 163, 175 and 194 Myr ago, we have made a new correlation with the galactic time series, finding $r = 0.994$ and, for the matched time intervals, $t = 4.94$ with 7 d.f., for which $P < 0.01$. Thus, the two series are strongly correlated, but in this case they have significantly different averages of the time intervals.

Note that the statistical tests in our original paper were not central to the search for periodicities or the physical arguments there. The approximate periodicity that appeared in both of our listed time series was formally detectable because the variance of the distribution of time intervals in each series was sufficiently small.

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Hund's rule

BOYD[1] recently suggested an explanation of Hund's rule in terms of electron correlation. A previous investigation of this approach[2] gave rise to a richer interpretation of two-electron spectra in terms of an alternating rule, in place of the usual Hund rule first noted by Russell and Meggers[3] for the spectrum of scandium. The alternating rule states that, within a given configuration, the energy ordering of singlet and triplet states reverses each time the angular momentum changes by one unit. For the term of greatest angular momentum, the triplet lies lowest. The rule reliably orders singlet-triplet energy levels in ~90% of known cases.

The alternating rule follows from the assumption that the state with the larger average value of the inter-electronic angle, θ_{12}, has less shielding and therefore a lower energy. This is not far from Boyd's approach. One might expect a triplet always to have less shielding, owing to the Fermi hole, but wavefunction antisymmetry can give rise to features in the singlet which resemble the triplet hole[2]. As the charge density $\rho(\theta_{12})$ has been found to obey the alternating rule[2], the Fermi hole argument is too simplistic.

The alternating rule helps in explaining cases deviating from Hund's first rule, but many exceptions are known. When the second rule fails, a singlet can be the lowest term in a configuration. An example is the 2p3d configuration of carbon, where the ^{1}D lies below the ^{3}F, contrary to Hund's first rule. The alternating rule, however, is obeyed: the ^{1}D lies below the ^{3}D, and the ^{3}F is below the ^{1}F. For the npn'd configuration, Hund's rules work only in ~50% of the cases[2] and many of the exceptions may be caused by a failure of Hund's second rule.

Recent studies of electron distributions in two-electron atoms[4,5] are beginning to yield a new and more comprehensive picture. Some states, for example, the doubly-excited states of helium-like atoms, exhibit very strong angular correlations, much greater than in singly-excited states, to the extent that collective, quasi-molecular quantization, with near-rigid rotations and bending and stretching vibrations, describes the electron distribution. Even the alkaline-earth atoms and alkali negative ions show considerable A—B—A molecular behaviour, although these systems have less rigid structures than He**.

That radial correlation sometimes dominates the energy orderings is difficult to reconcile with shielding concepts[2]. The 2s3s states of helium have similar angular electron distributions, much like that of the 2s^2, ^{1}S state, but the radial distributions are all quite different. Both the 2s3s states have strong angular correlation expected for a linear quasi-molecular system, with $\rho(\theta_{12})$ centred around π. The triplet corresponds to one quantum of excitation in the antisymmetric stretching mode for the A—B—A molecule; it has a lower energy than the singlet because the antisymmetric stretching has a lower frequency when A is lighter than B. The 2s2p, ^{3}P helium state, with a strong maximum in $\rho(\theta_{12})$ near π, corresponds to the first-excited rotor state, with no bending excitation. The angular distribution in the 2s2p, ^{1}P state is very different, with the maximum at slightly more than $\pi/2$, and with finite probability density at $\theta_{12} = 0$. This singlet is one of two partners in a nearly degenerate pair with one quantum in the bending vibration; the other is the lower energy 2p^2, ^{3}P, having almost the same angular distribution, but no electron density at $\theta_{12} = 0$.

In the quasi-molecular picture, the appropriate comparisons, as exemplified above, may be between states of different configurations. When electron correlation and configuration interaction are large, it is inappropriate to classify states in terms of a one-electron configuration, and Hund's rule loses its meaning. Nevertheless, it is interesting to ask under what circumstances a shielding argument can predict the energy orderings. The alternating rule has many exceptions for the npn'd, P and D terms, and future considerations of this problem should perhaps focus on physical interactions, such as collective motion kinematics and shielding, rather than on quantum numbers associated with a specific model and representation.

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Frost rings in trees and volcanic eruptions

LAMARCHE and Hirschboeck[1] find good agreement between the timing of notable frost events in the western United States and the occurrence of major volcanic eruptions worldwide from AD 1500 onwards. Notable frost events are defined as those damaging trees (seen in tree rings) at two or more localities or in 50% or more of sampled trees in any one locality. For the periods 1882–1968 and 1500–1880 they find, by considering coincidences of these phenomena in 3-yr segments, χ^2-values of 16.0 and 14.7, respectively, in frost versus volcano contingency tables, indicating significance at the 99.95% confidence level.

I have the following comments to make: a recomputation of χ^2 is possible using only the occasions (underlined in Table 1 of ref. 1) of geographically-widespread frost damage (that is, in both the Great Basin and the Rocky Mountains regions, >10° longitude apart). The results are: 1881 onwards, $\chi^2 = 6.7$, just significant at 99% confidence level; 1500–1880, $\chi^2 = 7.8$, significant at 99% confidence level.

The authors' selection of volcanic events, after Lamb[2], appears to be inconsistent at a few points. In general, they selected events printed[2] in bold type, indicating a consensus among compilers as to the importance of the events, with DVI/$E_{max} \geq 1{,}000$ for the eruption or combined eruptions. Events, with the latter parameter in bold type and ≥1,000 but with the name of the event in normal type (for example, Pogrumni, 1795), were omitted. To have followed this objective procedure consistently would have been acceptable but the following deviations were noted in particular: (1) Awu and Gunung (both 1641, combined DVI/$E_{max} = 1{,}500$) were omitted. (2) The 1785 eruption of Vesuvius was not assigned a DVI by Lamb and should have been omitted. (3) Hekla (1845) and Amargura (1846) (combined DVI/$E_{max} \simeq 1{,}800$) were omitted. (4) A group of four eruptions (1886–88) (combined DVI/$E_{max} = 1{,}100$ (estimated)[2] in 1888–90) was omitted. Item (2) will not affect the authors' results because Vesuvius was grouped with other eruptions, themselves with DVI/$E_{max} > 1{,}000$. However, according to Table 1 in ref. 1, the events in (1), (3) and