14. van der Heuvel, E. P. J. in *Planets Around Pulsars, Astr. Soc. Pacif. Conf. Ser. 36* (eds Phillips, J. A., Thorsett, S. E. & Kulkarni, S. R. 123–147 (Astr. Soc. Pacif., San Francisco, 1993).
15. Trager, S. C., Djorgovski, S. G. & King, I. R. in *Structure and Dynamics of Globular Clusters, Astr. Soc. Pacif. Conf. Ser. 50* (eds Djorgovski, S. G. & Meylan, G.) 347–355 (Astr. Soc. Pacif., San Francisco, 1993).
16. Phinney, E. S. in *Planets Around Pulsars, Astr. Soc. Pacif. Conf. Ser. 36* (eds Phillips, J. A., Thorsett, S. E. & Kulkarni, S. R.) 141–169 (Astr. Soc. Pacif., San Francisco, 1993).

ACKNOWLEDGEMENTS. We thank A. Fruchter, A. Lyne, S. Sigurdsson and S. Thorsett for discussions. The 42-m telescope is operated by the National Radio Astronomy Observatory under a cooperative agreement with the US National Science Foundation.

The origin of Pluto's peculiar orbit

Renu Malhotra

Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, Texas 77058, USA

THE origin of Pluto's unusual orbit—the most eccentric and inclined of all the planets—remains a mystery. The orbits of Pluto and Neptune overlap, but close approaches of these two planets are prevented by the existence of a resonance condition[1]: Pluto's orbital period is exactly 3/2 that of Neptune, which ensures that the conjunctions always occur near Pluto's aphelion. Long-term orbit integrations[2–5] have uncovered other subtle resonances and near-resonances, and indicate that Pluto's orbit is chaotic yet remains macroscopically stable over billion-year timescales. A suggestion[4] that the orbit may have evolved purely by chaotic dynamics appears unlikely in light of recent orbital stability studies[6], unless one appeals to a well-timed collision to place Pluto in its stable orbit[19]. Here I show that Pluto could have acquired its current orbit during the late stages of planetary accretion, when the jovian planets underwent significant orbital migration as a result of encounters with residual planetesimals[7]. As Neptune moved outwards, a small body like Pluto in an initially circular orbit could have been captured into the 3:2 resonance, following which its orbital eccentricity would rise rapidly to its current Neptune-crossing value.

Consider a mass m_e of planetesimals ejected to Solar System escape orbits by a planet of mass M at orbital radius r. From conservation of angular momentum, it follows that the planet suffers a decrease of orbital angular momentum and a concomitant decrease of orbital radius given by

$$\delta r/r \approx -2(\sqrt{2}-1)m_e/M \qquad (1)$$

For planetesimals that are scattered outwards away from the Solar System but do not achieve escape orbits (remaining bound in the Oort cloud of comets which exists as a halo surrounding our planetary system at distances greater than 20,000 astronomical units (AU)), the numerical factor in equation (1) would be slightly smaller. Conversely, planetesimals scattered into the inner Solar System increase the orbital radius and angular momentum of the planet. The four jovian planets acting together, however, behave counter to this simple picture. Consider planetesimal scattering by Neptune: those planetesimals scattered outwards end up in the Oort cloud, or return to be re-scattered. A fraction of the latter set is scattered inwards. The inwardly scattered planetesimals are systematically ejected from the planetary system by the more massive Jupiter. Thus the outer, less massive planets, Neptune and Uranus, transfer control of the ejection process to the inner, more massive Jupiter and Saturn. (Note that Pluto's small mass—only two-thousandths of the Earth's mass—makes it an ineffective scatterer of planetesimals.) Numerical simulations of this process show that Neptune, Uranus and Saturn suffer a net gain of angular momentum while Jupiter suffers a net loss[7].

The timescale and extent of the radial migration of the planets is determined by the details of the late stages of the planet formation process and is poorly constrained by current theories. The mass of the Oort cloud, which is believed to have been populated by small bodies ejected from the zones of the jovian planets, is estimated to be $\sim 10\,M_\oplus$ ($M_\oplus$ = mass of the Earth) (ref. 8). The ejection of such a mass of planetesimals corresponds to an inward migration of Jupiter of a few tenths of an AU, and an outward migration of Neptune of several AU. In the final stages of planet formation, ejection and accretion of planetesimals will occur concurrently; therefore, the timescale for the radial migration of the planets is expected to be comparable to that of accretion. An approximate lower limit for the latter is the observed $\sim 10^7$ yr lifetime of dust in disks around pre-main-sequence stars[9].

One consequence of Neptune's orbital expansion is that its orbital resonances would have swept across a range of heliocentric distances comparable to its radial migration. During this resonance sweeping, a small body such as Pluto, initially in a nearly circular orbit beyond Neptune, would have a significant probability of being captured into a resonance. Resonant perturbations from Neptune would transfer sufficient angular momentum to the body to keep it trapped in the resonance and to expand its orbit in concert with Neptune. A by-product of such a resonance capture is that Pluto's orbital eccentricity would have been excited to a high value. This may be seen by considering the perturbation equations in the restricted three-body approximation[10]. Near a $j{:}j+1$ resonance (where j is an integer), the resonant perturbations from Neptune on Pluto's orbital frequency, n_P, and eccentricity, e_P, are described by the following equations:

$$\dot{n}_P = 3(j+1)\mu_N n_P^2 e_P f(\alpha)\sin\phi$$
$$\dot{e}_P = -\mu_N n_P f(\alpha)\sin\phi \qquad (2)$$

where the 'resonance angle' is defined by

$$\phi = (j+1)\lambda_P - j\lambda_N - \tilde{\omega}_P \qquad (3)$$

λ denotes the mean longitude, $\tilde{\omega}$ is the longitude of perihelion, μ_N is the mass of Neptune relative to the Sun, $\alpha = a_N/a_P < 1$ is the ratio of the semimajor axes of Neptune and Pluto, and $f(\alpha)$ is a positive function, with numerical value 2.48 at the 3:2 resonance. Let $\langle \dot{n}_N \rangle$ be the mean rate of change of Neptune's orbital frequency as its orbit expands. Upon capture into resonance, the orbital frequency of Pluto becomes locked to that of Neptune, that is

$$(j+1)\langle \dot{n}_P \rangle \approx j\langle \dot{n}_N \rangle \qquad (4)$$

It then follows from equations (2) and (4) that

$$\left\langle \frac{de_P^2}{dt} \right\rangle \approx -\frac{2}{3(j+1)} \left\langle \frac{\dot{n}_N}{n_N} \right\rangle = \frac{1}{(j+1)} \left\langle \frac{\dot{a}_N}{a_N} \right\rangle \qquad (5)$$

where the last expression follows from the keplerian relation between the orbital frequency and the semimajor axis ($n^2a^3 =$ *constant*). In other words, upon capture into resonance, Pluto's eccentricity would increase at a rate determined by the average rate of expansion of Neptune's orbit. Equation (5) can be integrated to yield

$$e_{P,\text{final}}^2 - e_{P,\text{initial}}^2 \approx \frac{1}{j+1} \ln\left(\frac{a_{N,\text{final}}}{a_{N,\text{initial}}}\right) \qquad (6)$$

Neptune's current semimajor axis is $a_{N,\text{final}} = 30.17$ AU. Thus, we deduce that in order to excite Pluto's eccentricity from near-zero to 0.25, $a_{N,\text{initial}} \approx 25$ AU is required at the time of Pluto's capture into the 3:2 Neptune resonance ($j=2$ in equation (6)); Pluto's initial orbital radius would have been 32.8 AU. Remarkably, this result is independent of the timescale (and other details) of the expansion of Neptune's orbit. But there exists a practical constraint on the orbit expansion timescale, namely that it be much longer than the period of the resonant perturbations, in order that resonance capture be effected[11]. This lower limit on the orbit expansion timescale is $\sim 10^5$ yr.

The above analysis is based on first-order perturbation theory, and it is legitimate to question its validity, particularly in view of the fact that at the high eccentricity of 0.25, Pluto's orbit would become Neptune-crossing. Furthermore, the perturbations from the other jovian planets on Pluto (as well their mutual interactions) have been neglected in this analysis. In order to test the hypothesis more rigorously, we have carried out a numerical integration of the orbit evolution of the four jovian planets and Pluto. As Pluto's mass is several orders of magnitude smaller than the jovian planets, we treated it as a massless 'test particle'. The numerical method used was a modified version of the mixed-variable-symplectic method[12-14], which is a very fast integrator particularly suited to Solar System integrations.

I assumed a simple model for the time variation of the orbital semimajor axes of the outer planets:

$$a(t) = a_f - \Delta a e^{-t/\tau} \qquad (7)$$

where a_f is the value at the current epoch and τ is the orbit expansion timescale. I chose $\Delta a = 0$, 1, 3 and 6 AU for Jupiter, Saturn, Uranus and Neptune, respectively, consistent with the net migration induced by the ejection of a few $M_\oplus$ of planetesimals from the outer planetary region. This orbital migration was modelled in the equations of motion by means of a force of magnitude $f = f_0 e^{-t/\tau}$ on each planet along the direction of its velocity. (f_0 can be related in a straightforward manner to a_f, Δa and τ.) So that the simulation would use a reasonable amount of computer time, the total integration time was 20 Myr, and τ was chosen to be 1.5 Myr. The qualitative behaviour is expected to be insensitive to τ for $\tau \gtrsim 10^5$ yr, which ensures an approximate adiabatic condition for the evolution near the 3:2 Neptune resonance.) Twenty 'test particle' Plutos were integrated along with the planets. Their initial orbital elements were chosen randomly as follows: a in the range 32.5–33.5) AU (just outside the 3:2 Neptune resonance), e in the range 0.0–0.3, i in the range 0°–10°, and the angles (mean longitude, longitude of perihelion and ascending node) in the range 0–2π.

A typical case of the evolution found in the simulations is shown in Fig. 1. Nineteen of the 20 test Plutos were captured in the 3:2 resonance and the evolution proceeded in a manner very similar to that predicted by the simple analysis. (The one test Pluto that did not follow this evolution was captured in a 4:3 resonance and eventually had a close encounter with Neptune.) The behaviour of Pluto's a and e varied very little amongst the 19 cases, but the inclination evolution was rather sensitive to the initial conditions. The behaviour of the resonance angle ϕ was very stable; the final amplitude of its oscillations was found to be distributed in the range 30°–100°). (The observed value is 76°; recent numerical integrations[15] show that the long-term stability of the resonance requires a value <80°.) We conclude that the analytical argument above does capture the salient features of the dynamical evolution. The long-period variations, evident particularly in the inclination, are possibly due to a nearby inclination-type secular resonance[16]. Longer integrations are required to determine the range of behaviours possible for Pluto's inclination.

A few words about the evolution of the jovian planets are in order. Although the initial orbits of the planets were significantly different from their current orbits, the behaviour of the orbital eccentricities and inclinations found in the simulations was similar to that observed in the long time integrations of the current planetary configuration[3].

The scheme outlined here for the origin of Pluto's highly eccentric, Neptune-crossing orbit is quite robust in that the probability of capturing Pluto in the 3:2 Neptune resonance from an initially circular orbit is very high. However, there are a few points of note. (1) I have modelled the radial migration of the jovian planets as a smooth process, whereas in reality it is stochastic. We expect that, as long as no single event produces too large a change in the planetary orbits, the smooth approximation should work well. A rough estimate for the mass of an ejected planetesimal that would invalidate this assumption can be obtained by equating the change in the orbital radius, $|\delta r/r|$ (Equation 1), with the half-width of the 3:2 Neptune resonance, $\delta a_P/a_P \approx 4(\mu_N f(\alpha) e_P/3)^{1/2}$ (ref. 11); this yields a mass $m_c \sim 10^{27}$ g, which is two orders of magnitude greater than the mass of Pluto. Thus, if we consider that Pluto was among the largest members of the planetesimal population beyond the orbit of Neptune surviving to the evolutionary stage considered here, then the smooth approximation appears quite reasonable. (2) In the numerical simulations, I assumed that the masses of the jovian planets were fixed at their current values during the entire evolution. The probability of resonance capture will depend upon the mass of Neptune. However, for sufficiently slow expansion of the planet orbits, resonance capture theory shows that the dependence on the mass of the perturbing planet is not very strong[11]. Therefore this limitation of the simulations is not likely to be of great import. (3) The analysis given here shows that the most direct requirement is on Neptune's orbital migration: $\Delta a_N \gtrsim 5$ AU. The sensitivity of the dynamics to the Δas of the other planets remains to be determined. The values chosen in

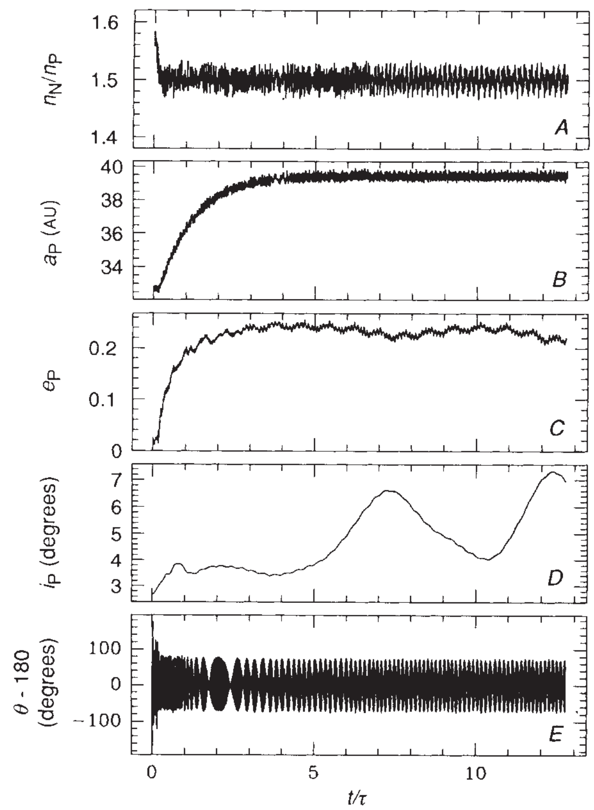


FIG. 1 The time evolution of Pluto's orbital elements is shown for a typical case of the capture of Pluto into the 3:2 Neptune resonance. (The time is indicated in units of τ, the characteristic timescale for the expansion of Neptune's orbit.) As Neptune's orbit evolves outward, the mean motion ratio (*A*) decreases initially until it reaches the value 3/2; at this point Pluto is captured in the resonance and subsequently its orbit also expands (*B*) in concert with Neptune. Pluto's eccentricity is pumped up rapidly (*C*) to a Neptune-crossing value. The evolution of the inclination (*D*) appears to be dominated by a nearby secular resonance, but remains to be understood. The resonance angle goes from circulations to remarkably constant-amplitude librations (*E*).

my simulation ensure that during their radial migration, the jovian planets do not encounter any strong orbital resonances amongst themselves, and therefore suffer only relatively small mutual perturbations. How restrictive this condition might be on the entire dynamical evolution described here requires further study. (4) Finally, the role of possible planetesimal collisions with Pluto during its evolution in the 3:2 Neptune resonance also needs to be evaluated. This may have an important bearing on the origin and properties of the Pluto–Charon binary.

The significant orbital evolution of the jovian planets implied by the model outlined here would have implications for a number of other problems concerning the outer Solar System, such as the capture of Triton by Neptune[17] and the structure of the putative Kuiper belt[18], as well as for studies of the evolution of the asteroid belt. □

Received 5 July; accepted 6 September 1993.

1. Cohen, C. J. & Hubbard, E. C. *Astr. J.* **70**, 10–13 (1965).
2. Williams, J. G. & Benson, G. S. *Astr. J.* **76**, 167–177 (1971).
3. Applegate, J. H., Douglas, M. R., Gursel, J., Sussman, G. J. & Wisdom, J. *Astr. J.* **92**, 176–194 (1986).
4. Sussman, G. J. & Wisdom, J. *Science* **241**, 433–437 (1988).
5. Milani, A., Nobili, A. M. & Carpino, M. *Icarus* **82**, 200–217 (1989).
6. Levison, H. F. & Duncan, M. J. *Astrophys. J.* **406**, L35–L38 (1993).
7. Fernandez, J. A. & Ip, W. H. *Icarus* **58**, 109–120 (1984).
8. Weissman, P. R. *Nature* **344**, 825–830 (1990).
9. Strom, S. E., Edwards, S. & Strom, K. M. in *The Formation and Evolution of Planetary Systems* (eds Weaver, H. A. & Danly, L.) 91–107 (Cambridge Univ. Press, 1989).
10. Brouwer, D. & Clemence, G. M. *Methods of Celestial Mechanics* (Academic, New York, 1961).
11. Dermott, S. F., Malhotra, R. & Murray, C. D. *Icarus* **76**, 295–334 (1988).
12. Wisdom, J. & Holman, M. *Astr. J.* **102**, 1528–1538 (1991).
13. Saha, P. & Tremaine, S. *Astr. J.* **104**, 1633–1640 (1992).
14. Malhotra, R. *Celestial Mech. and Dynamical Astr.* (submitted).
15. Levison, H. F. & Stern, S. A. *Lunar planet. Sci.* **24**, 869–870 (1993).
16. Knezevic, Z., Milani, A., Farinella, P., Froeschle, Ch. & Froeschle, Cl. *Icarus* **93**, 316–330 (1991).
17. McKinnon, W. B. *Nature* **311**, 355–358 (1984).
18. Duncan, M. J. & Quinn, T. *A. Rev. Astr. Astrophys.* **31**, 265–295 (1993).
19. Levison, H. F. & Stern, S. A. in *Pluto–Charon Conf.*, 6–9 July 1993, Flagstaff, Arizona, USA.

ACKNOWLEDGEMENTS. I thank S. Dermott, A. Milani and A. Nobili for discussion, M. Duncan for computer programs, and P. Goldreich for comments on a preliminary draft of this letter. This work was supported by NASA.

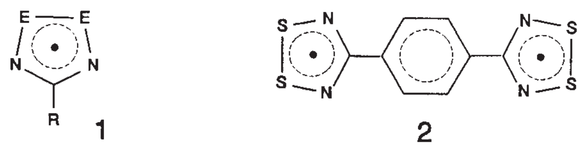
Conducting charge-transfer salts based on neutral π-radicals

C. D. Bryan*, A. W. Cordes*, R. M. Fleming†, N. A. George‡, S. H. Glarum†, R. C. Haddon†, R. T. Oakley‡, T. T. M. Palstra†, A. S. Perel†, L. F. Schneemeyer† & J. V. Waszczak†

* Department of Chemistry and Biochemistry, University of Arkansas, Fayetteville, Arkansas 72701, USA
† AT&T Bell Laboratories, Murray Hill, New Jersey 07974-0636, USA
‡ Guelph-Waterloo Centre for Graduate Work in Chemistry, Guelph Campus, Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario N1G 2W1, Canada

MOST molecular conductors rely on charge transfer to create carriers. For example, the ET salts[1] are hole-doped whereas the C_{60} salts[2] are electron-doped. Neutral radical species in which bands are formed by π-orbital overlap would be expected to have half-filled bands and thus to be conducting[3], but no such metals have yet been reported. Here we report the synthesis and characterization of a molecular conductor which combines both of these approaches: energy bands are formed from one-dimensional stacks of neutral π-radicals, and the material is rendered conducting by electron transfer from the conduction band following doping with an acceptor. The radical species is the 1,4-phenylene-bis(dithiadiazolyl) diradical 1,4-[$(S_2N_2C)C_6H_4(CN_2S_2)$] (2 in Fig. 1), reaction of which with iodine vapour leads to crystals of [2][I]. At low temperatures this compound is essentially a diamagnetic insulator, but above 200 K the conductivity and magnetic susceptibility increase markedly, and at room temperature the conductivity reaches 100 S cm^{-1}, which is comparable to that shown by conventional molecular charge-transfer salts.

The preparation of synthetic conductors usually involves the oxidation or reduction of a closed-shell molecule to generate a mixed-valence or charge-transfer salt[1,2]. We have been interested in an alternative approach, namely the use of neutral π-radicals, in which the requirement for a partially filled energy band is inherently fulfilled[3]. There are, however, few π-radicals with sufficient stability and flexibility[4–6]. Initially we examined variants of the phenalenyl radical[7–10], but recent advances in heterocyclic chemistry have provided a variety of potentially useful π-radical building blocks[11,12]. One objective has been to generate



1 2

FIG. 1 The molecular structures of the neutral radical dithiadiazolyl (1), where E is S or Se, and the 1,4-phenylene-bis(dithiadiazolyl) diradical (2).

materials consisting of molecular stacks or columns, and for several choices of the R-group in 1 (Fig. 1, E = S, Se), this packing arrangement has been realized[11,13]. By definition, however, neutral radicals give rise to a half-filled electronic energy band, which in a one-dimensional packing arrangement is prone to a Peierls instability (essentially a dimerization process) driven by charge density waves (CDWs). Because the radicals tend to dimerize, we have attempted to stabilize the metallic state by applying pressure and by preparing materials in which two- and three-dimensional interactions are enhanced. Several small-band-gap semiconductors of this kind (with E = Se) have been characterized[11,13,15], but no truly metallic compound has yet been realized.

An alternative strategy for stabilizing the metallic state involves doping the energy band away from the half-filling which is characteristic of the neutral state. We have now found that the oxidation of the 1,4-phenylene-bridged bifunctional radical 2 (Fig. 1, ref. 14) with iodine produces a highly conductive mixed-valence salt of formula [2][I]. The preparation requires heating a mixture of 2 (1.0 mmol) and I_2 (0.5 mmol) in a sealed, evacuated (1 mTorr) pyrex tube (25 × 250 mm). Slow fractional sublimation along a temperature gradient (225 °C to 160 °C over 100 mm) affords, after several days, lustrous silver black needles with elemental composition $C_8H_4N_4S_4I$ (yield ~70%).

The crystal structure (Fig. 2) consists of columns of uniformly spaced (3.415(2) Å) molecules of 2 interspersed by columns of disordered iodines running along the *x*-axis. Perpendicular to the stacking direction the heterocyclic rings lie in dove-tailed arrays running parallel to the *y*-axis. Within the CN_2S_2 rings, the S–S (2.066(1) Å) and S–N (1.616(2) Å) bonds are between those seen in the neutral dimer of 2 (ref. 14) and its di-cation $[2]^{2+}$ (ref. 15), but closer to the former, implying an oxidation state (per ring) of <0.5.

The magnetic susceptibility of [2][I] was determined between 4 K and the decomposition point using the Faraday technique (Fig. 3). At low temperatures there is a small Curie tail due to