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Pressure dependence of the mean excitation energy of atomic systems

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Abstract

Changes in the mean ionization energy of atoms in compressed matter are estimated through cage models of atomic confinement whereby pressure is obtained in terms of the rate of change of total atomic energy with volume. Resort is taken to a recently implemented shellwise Thomas–Fermi–Dirac–Weizsacker theory for confined atoms to construct the atomic energy functional, which is self-consistently optimized for different confinement conditions. The resulting modified atomic orbital densities are then used within the Local Plasma Approximation to evaluate the corresponding orbital and total mean excitation energies. Good agreement is obtained with accurate calculations for free atoms. For compressed atoms agreement is found with a previously derived universal expression [J.M. Peek, Phys. Rev. A 36 (1987) 5429] for total mean excitation energies suggesting its adequacy for this class of studies.

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1. Introduction

Theoretical predictions [1,2] of differences in the stopping and range of heavy ions traversing a material subject to high pressures as compared to the case of normal pressure indicate an important

effect in the stopping dynamics mainly due to the pressure dependence of the atomic mean excitation function in addition to corresponding changes in the target bulk properties. The relevance of this class of studies may be directly related with ranges of fission fragments in highly compressed fissile targets [1] and geothermometry experiments on the role of pressure to stop the normal process of length shrinkage of fission fragment tracks in materials extracted from deep boreholes in the

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earth crust (e.g. fluoroapatite), during isochronal thermal annealing in the laboratory [3]. It is well known that the inelastic energy loss process between a bare charged projectile and a target atom or molecule has its origin in the energy transfer to the internal degrees of freedom of the target material which are accounted for through an excitation function. According to Bethe's original work, the electronic stopping cross section (S_e) of a swift bare ion of charge Z_1 and velocity v is given as [4]

$$S_e(v) = \frac{4\pi Z_1^2 Z_2 e^4}{mv^2} \ln \left(\frac{2mv^2}{I_0} \right), \quad (1)$$

where Z_2 is the number of electrons composing the atomic scatterer and m and e the electron mass and charge, respectively. I_0 in Eq. (1) is the logarithmic mean excitation energy defined as [5]

$$Z_2 \ln I_0 = \sum_n f_{n0} \ln(E_n - E_0), \quad (2)$$

with f_{n0} being the dipole oscillator strength for the transition from the ground-state energy E_0 to a state of energy E_n and the sum involving all discrete and continuum states. Formally, I_0 is evaluated in terms of the dipole oscillator strength (DOS) sums [6,7] yielding accurate predictions as compared to experiment. However, the actual theoretical computation of DOS requires a difficult and complicated process involving well defined ab initio methods to construct accurate atomic and molecular wavefunctions [7].

A useful alternative means to evaluate I_0 is the Local Plasma Approximation (LPA) [8] whereby the dynamical response of an atom in the stopping medium is characterized by the plasma oscillation of the electron cloud. Considering the atom as an inhomogeneous electron gas with local electron density $\rho(\mathbf{r})$ the local plasma frequency $\omega_p(\mathbf{r})$ is given as

$$\omega_p(\mathbf{r}) = [4\pi e^2 \rho(\mathbf{r})/m]^{1/2}. \quad (3)$$

Within this approximation, the atomic mean excitation energy is given as

$$Z_2 \ln I_0 = \int \rho(\mathbf{r}) \ln[\gamma \hbar \omega_p(\mathbf{r})] d^3\mathbf{r}, \quad (4)$$

with γ an empirical parameter introduced to account for polarization effects in single-particle

excitations. This parameter has been generally chosen as $\gamma = 1$ for light atoms, where polarization effects are not so important, and $\gamma = \sqrt{2}$ for heavier atoms (for a review, see [9]).

A major advantage of the LPA is its representation in terms of the electronic density whose changes in matter under high pressures may render changes in the mean excitation energy and consequently in S_e . The aim of this work is to study these changes by resorting to the LPA and a model of atomic confinement whereby pressure, energy and electron density are obtained self-consistently.

2. Theory

2.1. Pressure and the confinement model

The effect of pressure on the ground-state electronic and structural properties of atoms and molecules have been widely studied through quantum confinement models [10] whereby an atom (molecule) is enclosed within e.g. a spherical cage of radius R with infinitely hard walls. In this class of models, the ground-state energy evolution as a function of confinement radius renders the pressure exerted by the electronic density on the wall as $P = -\partial E/\partial V$. For atoms confined within hard walls, as in this case, pressure may also be obtained through the virial theorem [11]:

$$P(R) = \frac{E(R) + K(R)}{3V}, \quad (5)$$

with R the cage radius, V its volume and $E(R)$, $K(R)$ the corresponding total ground-state electronic and kinetic energy, respectively, which are self-consistently obtained for each cage radius. The energy dependence on cage radius is obtained in this work through a recently developed shellwise implementation of the Thomas–Fermi–Dirac–Weizsacker (TFDW) density functional theory for confined atoms [12]. The relevant ideas are stated here in a condensed manner.

Let $E_{\text{TFDW}}(\rho, R, \lambda)$ denote the TFDW energy-density functional for the neutral atom inside a spherical cage of radius R , where ρ stands for the total electron density and λ is a scaling parameter for the Weizsacker inhomogeneity correction [13].

It is well known that the Thomas–Fermi electron gas model for the atom does not account for shell structure. However, Wang and Parr [14] and others [15] have shown that, when the electron density is introduced in $E_{\text{TFDW}}(\rho, R)$ in an ad hoc manner to account for the shellwise structure, the optimized energies and resulting atomic densities correspond reasonably well to the Hartree–Fock values. Within this spirit, we write the atomic electronic density, ρ , as the sum of orbital densities, ρ_i :

$$\rho = \sum_i \rho_i(r, R, \xi_i), \quad (6)$$

with

$$\rho_i(r, R, \xi_i) = N_i r^{2n_i-2} e^{-2\xi_i r} (1 - r/R), \quad (7)$$

where n_i is the principal quantum number of orbital “ i ”, ξ_i the corresponding orbital parameter and N_i the relevant normalizing constant such that the orbital population ω_i satisfies the condition

$$\int_{\Gamma} \rho_i(r, R, \xi_i) d\tau = \omega_i, \quad (8)$$

where Γ indicates the domain of integration within the confinement volume.

Note that the term in parenthesis in Eq. (7) guarantees that the orbital density (and total density) vanishes at the boundary of the confining volume.

Using Eqs. (6)–(8) for each value of R , the optimized energy and orbital parameters ξ_i are obtained by requiring that

$$\left(\frac{\partial E_{\text{TFDW}}(\rho, R, \lambda)}{\partial \xi_i} \right)_R = 0. \quad (9)$$

The parameter λ has been set in this work as $\lambda = 1/8$ after a systematic energy optimization [12] for first and second row atoms yielding energy values close to the Hartree–Fock ones for free [16] and confined [17] atoms. For this reason, in the subsequent discussion the energy-density functional employed here will be referred to as TFD($\frac{1}{8}$)W.

2.2. Pressure effects on the mean excitation energy

The energy optimization procedure indicated by Eq. (9) implies a change in the orbital parameters ξ_i

and consequent change of the electron density as pressure increases. Accordingly, the LPA as given by Eqs. (3) and (4) will reflect corresponding changes in the total mean excitation energy. Moreover, the orbital treatment of the TFD($\frac{1}{8}$)W functional allows to estimate the changes in orbital densities and hence changes in orbital mean excitation energies. Following the orbital local plasma approximation (OLPA) [18,19] the total mean excitation energy given by Eq. (4) may be expressed as

$$\ln I_0 = \frac{1}{Z_2} \sum_i \omega_i \ln I_i, \quad (10)$$

where the mean excitation energy of orbital “ i ” is given as

$$\ln I_i = \frac{1}{\omega_i} \int \rho_i(\mathbf{r}) \ln \left[\hbar \gamma_i \left(\frac{4\pi e^2 \rho(r)}{m} \right)^{1/2} \right] d^3\mathbf{r} \quad (11)$$

and $\rho_i(\mathbf{r})$ is the local orbital electron density and $\rho(r)$ the angular average of local total electron density and γ_i the corresponding scaling parameter as proposed in the Lindhard–Scharff LPA theory. Since no specific criterion exists to assign a value to γ_i for each orbital, its value is chosen here as unity as done in [18,19] in order to avoid dependence of the theoretical predictions upon any ad hoc parameter.

The implementation of Eqs. (10) and (11) to the case of confined systems is straightforward by considering all integrals within the confinement domain Γ . This method has been successfully applied to the case of pressure effects in the core and bond contributions to proton stopping in molecular targets [20].

For purposes of comparison with other calculations, the set of calculated orbital mean excitation energies for atoms with $2 \leq Z_2 \leq 18$ were grouped in shell-like contributions as suggested by Chen et al. [21], i.e.

$$\ln I_S = \frac{1}{Z_S} \sum_i \omega_{iS} \ln I_{iS}, \quad (12)$$

where S stands for shell K, L, M; Z_S is the number of electrons in shell S and the sum is done over orbitals composing that shell with corresponding orbital population ω_{iS} and mean orbital excitation energy I_{iS} .

3. Results and discussion

The scheme discussed in the previous section has been applied to the calculation of the orbital and total mean excitation energies for free and confined atoms with $2 \leq Z_2 \leq 18$. Table 1 displays – as an example – the relevant quantities obtained in this work for oxygen, neon and chlorine, for a selected set of values of the confining radius. The last three columns in this table correspond to the free-atom case. To the authors' knowledge, this is the first time that the shellwise implementation of the TFDW density functional is applied to the calculation of orbital and total mean excitation energies. Hence, before discussing the pressure effects on mean excitation energies, let us first analyze the predictions of this work for the free-atom case and compare with available results in the literature.

Fig. 1 shows the mean excitation energies of the K, L and M shells as a function of atomic number obtained in this work (TFD $\frac{1}{8}$ W) (solid circles) as compared to accurate calculations by Oddershede and Sabin (OS) [7] using the DOS method (open squares), the original OLPA method developed by Meltzer et al. (MST) [18] based on the local spin density approximation to density functional theory (open diamonds) and the calculations by Chen et al. [21] using an analytical Moliere-type representation of the HFS densities and the original MST-OLPA method [18] (open circles). It seems clear from this figure that the predictions of the TFD $\frac{1}{8}$ W-based LPA method for the shell (and orbital) mean excitation energies are in reasonable agreement with the other – more elaborate – calculations. We note that all the OLPA-based calculations use $\gamma_i = 1$. Interestingly, the K-shell predictions of this work are overall in better agreement with the accurate DOS calculations by OS. This may be related with the adequate description of the TFD $\frac{1}{8}$ W cusp density at the origin for the 1s orbital [12]. The observed quantitative discrepancy between this work and the others in the case of the L-shell for Li, Be and B and in general for the M-shell remains still to be explained. In spite of this, the total mean excitation energies obtained through Eq. (10) show the right qualitative behavior and an improved quantitative trend over other

OLPA-based methods as may be verified from Fig. 2, where we have plotted the corresponding accurate values by OS and those by MST.

From the previous discussion we may deem the TFD $\frac{1}{8}$ W method as promising means to treat, with some confidence, the orbital and total mean excitation energies. We now turn our attention to the pressure effects on these quantities. Going back to the results shown in Table 1, we first notice an increasing value of the orbital mean excitation energies as pressure increases (confinement radius decreases). This behavior is observed for all, except the 3s orbital values in chlorine, which first show a slight increase from the free-case to moderate confinement and then diminishes. A careful analysis of the evolution of the mean excitation energy for this orbital indicates a monotonic increase for cage radii $R < 3.5$ a.u. This aspect, together with the already discussed overestimation of M-shell mean excitation energies for the free atoms are currently investigated. Interestingly enough, this anomaly seems to have no serious effect on the behavior of the total mean excitation energy as pressure increases, as may be verified from Table 1 and Fig. 3. In this figure we have plotted – as an example – the cage-radius dependence¹ of the total mean excitation energies for O (dotted curves), Ne (dashed curves) and Cl (continuous curves) obtained in this work as compared with corresponding values predicted by Peek [22] (triangles for O, circles for Ne and squares for Cl). The latter author developed a universal relation for I_0/Z for confined atoms using the original LPA with $\gamma = 1.41$ (Eqs. (3) and (4)) and the Thomas–Fermi equation for the radial density considering the nature of its solutions for neutral atoms of finite radius. Incidentally, this important seminal paper seems to have been unjustly undiscovered in the literature. Here we give it the merit it deserves. For purposes of comparison, we show in Fig. 3 our predicted I_0 values for $\gamma = 1$ and $\gamma = 1.41$.

As gathered from Fig. 3, the results of this work with $\gamma = 1$ compare more favorably, overall, with

¹ For discussion purposes we have chosen to use the cage radius in this figure and not the pressure, since pressure has different values for different atoms in the same confinement volume.

Table 1

Values of orbital parameters (ξ_i), orbital mean excitation energies (I_i), total mean excitation energy (I_0), pressure (P) and total energy (E) for O, Ne and Cl for selected values of cage radii (R)

Z	R (a.u.)	3.5		6.0		10		∞	
		$\xi(a_0^{-1})$	I_k (eV)						
8	1s	7.48560	424.79	7.53757	422.49	7.57140	422.22	7.61733	422.19
	2s	3.83399	105.83	3.97881	102.72	4.02111	102.24	4.06832	102.18
	2p	1.69786	38.45	1.58863	29.92	1.61667	28.97	1.66998	28.87
	I_0 (eV)	90.3		78.9		77.6		77.4	
	P (GPa)	135		2.5		0.03		0	
	$-E$ (eV)	2031.622		2046.609		2047.670		2047.752	
10	1s	9.53816	616.21	9.59099	613.73	9.62511	613.57	9.67089	613.56
	2s	5.31549	170.76	5.39984	166.92	5.43661	166.62	5.48314	166.58
	2p	1.97501	52.72	1.96439	46.92	2.00431	46.42	2.05597	46.34
	I_0 (eV)	109.3		101.2		100.4		100.3	
	P (GPa)	150		1.9		0.03		0	
	$-E$ (eV)	3476.786		3491.555		3492.426		3492.562	
17	1s	16.8858	1487.17	16.94100	1485.63	16.97310	1485.06	17.01840	1485.02
	2s	9.88483	479.21	9.98488	478.31	10.01490	477.86	10.06090	477.82
	2p	4.96131	218.74	4.98372	210.93	5.01509	209.94	5.06203	209.83
	3s	2.51103	51.71	3.21812	67.72	3.36418	69.46	3.41849	69.45
	3p	2.51924	51.99	2.01859	37.82	1.96129	28.59	2.00982	28.34
	I_0 (eV)	166.2		146.6		142.2		141.8	
	P (GPa)	440.4		11.6		0.14		0	
	$-E$ (eV)	12463.149		12515.291		12520.922		12521.248	

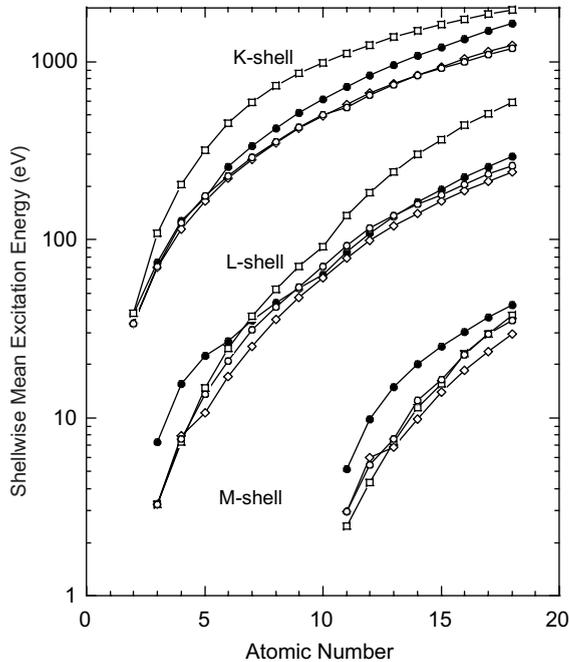


Fig. 1. Mean excitation energy (in eV) of the K, L and M shells for first and second row elements. Solid circles: this work (Eq. (12)). Open squares: obtained from oscillator strength calculations from [7]. Open diamonds: obtained from Eq. (12) and the OLPA values from [18]. Open circles: values reported in [21] using the OLPA [18] and a Moliere representation of HFS densities.

those predicted by Peek. This indicates that taking $\gamma = 1$ in our density functional approach constitutes a reasonable approximation, although the lack of experimental information on mean excitation energies for compressed target materials prevents us to assess a definite conclusion on this issue. The universal character of the relation obtained by Peek and its reasonable agreement with the TFD $\frac{1}{8}$ W method make the former a useful means to estimate total mean excitation energies for compressed atoms. It is important to observe that the agreement between both treatments is not obvious. The TFD $\frac{1}{8}$ W method consists on the energy optimization through an ansatz density function which is not solution of the Thomas–Fermi equation. Both treatments have in common the electron-gas expressions for the energy components and keep self-consistency through Poisson’s equation (a known requirement to derive the

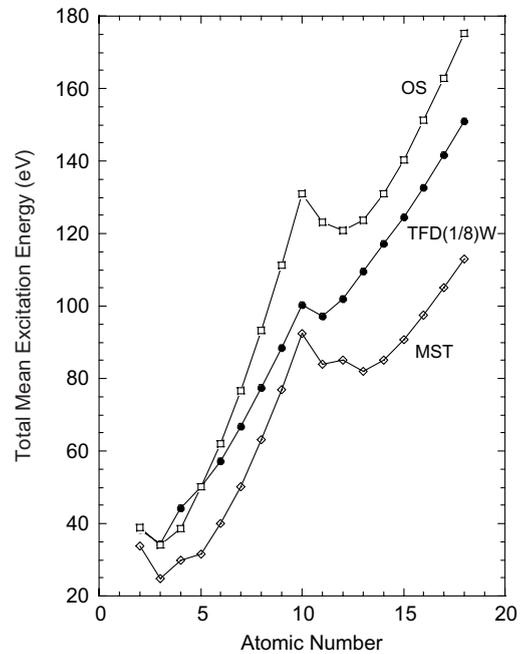


Fig. 2. Total mean excitation energies (in eV) for first and second row atoms. Solid circles: this work. Open squares: [7], oscillator strength calculation. Open diamonds: OLPA calculation from [18].

Thomas–Fermi equation from energy considerations). It is then remarkable that consistency is kept between both calculations.

4. Conclusions

Pressure effects on the orbital and total mean excitation energies have been studied using a shellwise implementation of the TFDW density functional method recently derived for confined atoms. For free atoms, a general agreement with accurate calculations is observed for inner-shell mean excitation energies whereas for the outermost shells the predicted mean excitation energies seem to be overestimated relative to the other methods. However, good agreement is observed for total mean excitation energies. For atoms under pressure, the total mean excitation energies obtained in this work show reasonable agreement with those obtained by Peek [22] thus giving support for the use of his universal relation to estimate

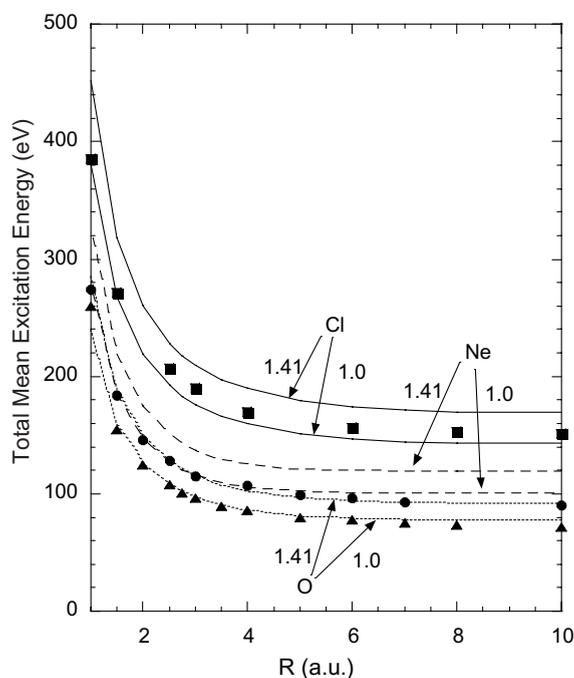


Fig. 3. Dependence of total mean excitation energy (in eV) for O (dotted curves), Ne (dashed curves) and Cl (continuous curves) as a function of radius of the confining cage for $\gamma = 1$ and $\gamma = 1.41$. Also included are the predictions from the universal model reported in [22] (triangles for O, circles for Ne and squares for Cl).

of pressure effects on the stopping total mean excitation energy. A major advantage of the $\text{TFD}_{\frac{1}{8}}\text{W}$ is its ability to explore shell structure contributions and yet keeping the characteristics for the study of compressed many-electron atoms.

References

- [1] R.A. Lewis, G.A. Smith, W.S. Toothacker, *Phys. Rev. A* 44 (1991) 392.
- [2] S.A. Cruz, *Nucl. Instr. and Meth. B* 222 (2004) 411.
- [3] A.S. Wendt, O. Vidal, L.T. Chadderton, *Earth Planet. Sci. Lett.* 201 (2002) 593;
- B.P. Kohn, D.X. Belton, R.W. Brown, A.J.W. Geadow, P.F. Green, J.F. Lovering, *Earth Planet. Sci. Lett.* 215 (2003) 299;
- O. Vidal, A.S. Wendt, L.T. Chadderton, *Earth Planet. Sci. Lett.* 215 (2003) 307.
- [4] H.A. Bethe, R. Jackiw, *Intermediate Quantum Mechanics*, third ed., Addison-Wesley, Massachusetts, 1997, Chapter 17.
- [5] J.R. Sabin, J. Oddershede, *Phys. Rev. A* 26 (1982) 3209.
- [6] M. Inokuti, J.L. Dehmer, T. Baer, J.D. Hanson, *Phys. Rev. A* 23 (1981) 95;
- J.L. Dehmer, M. Inokuti, R.P. Saxon, *Phys. Rev. A* 12 (1975) 102;
- M. Inokuti, T. Baer, J.L. Dehmer, *Phys. Rev. A* 17 (1978) 1229.
- [7] J. Oddershede, J.R. Sabin, *At. Data Nucl. Data Tables* 31 (1984) 275.
- [8] J. Lindhard, M. Scharff, K. Dan. *Vidensk. Selsk. Mat.-Fys. Medd.* 27 (15) (1953);
- J. Lindhard, K. Dan. *Vidensk. Selsk. Mat.-Fys. Medd.* 28 (8) (1954);
- J. Lindhard, M. Scharff, *Phys. Rev.* 124 (128) (1961).
- [9] E. Kamaratos, *Chem. Rev.* 84 (1984) 561.
- [10] W. Jaskólski, *Phys. Rep.* 271 (1996) 1;
- S.A. Cruz, J. Soullard, *Chem. Phys. Lett.* 391 (2004) 138.
- [11] R.F.W. Bader, M.A. Austen, *J. Chem. Phys.* 107 (1997) 4271;
- J.O. Hirschfelder, C.F. Curtiss, R.B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1964.
- [12] S.A. Cruz, C. Diaz-Garcia, G. Covarrubias, *Int. J. Quantum Chem.*, in press.
- [13] C.F.V. Weizsacker, *Z. Phys.* 96 (1935) 431.
- [14] W.P. Wang, R.G. Parr, *Phys. Rev. A* 16 (1977) 891.
- [15] E. Hernández, J.L. Gázquez, *Phys. Rev. A* 25 (1982) 107.
- [16] E. Clementi, C. Roetti, *At. Nucl. Data Tables* 14 (1974) 177.
- [17] E.V. Ludeña, *J. Chem. Phys.* 69 (1978) 1770.
- [18] D.E. Meltzer, J.R. Sabin, S.B. Trickey, *Phys. Rev. A* 41 (1990) 220;
- D.E. Meltzer, J.R. Sabin, S.B. Trickey, *Phys. Rev. A* 42 (1990) 666(E).
- [19] D.E. Meltzer, J.R. Sabin, S.B. Trickey, J.Z. Wu, *Nucl. Instr. and Meth. B* 82 (1993) 493.
- [20] S.A. Cruz, J. Soullard, *Adv. Quantum Chem.* 46 (2004) 195.
- [21] Y.F. Chen, C.M. Kwei, C.J. Tung, *J. Phys. B: At. Mol. Opt. Phys.* 26 (1993) 1071.
- [22] J.M. Peek, *Phys. Rev. A* 36 (1987) 5429.